



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C08F 299/08, A61K 7/06	A2	(11) International Publication Number: WO 93/23446 (43) International Publication Date: 25 November 1993 (25.11.93)
(21) International Application Number: PCT/US93/04429 (22) International Filing Date: 11 May 1993 (11.05.93) (30) Priority data: 07/883,974 15 May 1992 (15.05.92) US (71) Applicant: THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventors: TORGERSON, Peter, Marte ; 4127 U.S. Rt. 35 NW, Washington Ct. House, OH 43160 (US). BALCHU- NAS, Anthony, Thomas ; 5468 Yosemite Drive, Fair- field, OH 45014 (US).		(74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45202 (US). (81) Designated States: AU, BB, BG, BR, CA, CZ, FI, HU, JP, KP, KR, KZ, LK, MG, MN, MW, NO, NZ, PL, RO, RU, SD, SK, UA, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>Without international search report and to be republished upon receipt of that report.</i>
(54) Title: ADHESIVE AGENT CONTAINING POLYSILOXANE-GRAFTED POLYMER, AND COSMETIC COMPOSITIONS THEREOF (57) Abstract <p>Polymeric adhesive agents are disclosed which comprise polysiloxane grafted polymers wherein: (a) the polymers are made by polymerization of polysiloxane-containing monomers and non-polysiloxane-containing monomers, typically by free radical polymerization; (b) the adhesive agent has a weight average molecular weight of at least about 20,000 and contains from about 1 % to about 50 %, by weight, of polysiloxane-containing monomer; and (c) the weight percentage of silicon present as unreacted polysiloxane-containing monomer and silicone-grafted polymer having a viscosity at 25 °C of below about 10,000,000 centistokes based on the total silicon present as unreacted silicon monomer and polysiloxane-grafted polymer is about 15 % or less. Also, the adhesive agent contains no more than about 4 %, by weight, of unreacted polysiloxane-containing monomer and polysiloxane-grafted polymer having a viscosity at 25 °C of below about 10,000,000 centistokes. Cosmetic compositions containing such adhesive agents are also disclosed.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	MR	Mauritania
AU	Australia	GA	Gabon	MW	Malawi
BB	Barbados	GB	United Kingdom	NL	Netherlands
BE	Belgium	GN	Guinea	NO	Norway
BF	Burkina Faso	GR	Greece	NZ	New Zealand
BG	Bulgaria	HU	Hungary	PL	Poland
BJ	Benin	IE	Ireland	PT	Portugal
BR	Brazil	IT	Italy	RO	Romania
CA	Canada	JP	Japan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SK	Slovak Republic
CI	Côte d'Ivoire	LJ	Liechtenstein	SN	Senegal
CM	Cameroon	LK	Sri Lanka	SU	Soviet Union
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	MC	Monaco	TG	Togo
DE	Germany	MG	Madagascar	UA	Ukraine
DK	Denmark	ML	Mali	US	United States of America
ES	Spain	MN	Mongolia	VN	Viet Nam
FI	Finland				

- 1 -

ADHESIVE AGENT CONTAINING
POLYSILOXANE-GRAFTED POLYMER, AND
COSMETIC COMPOSITIONS THEREOF

5

TECHNICAL FIELD

The present invention relates to adhesive agents containing polysiloxane-grafted polymers and to compositions, such as cosmetic compositions, containing such adhesive agents. This invention especially relates to adhesive agents useful for hair setting purposes, and to hair setting compositions containing such adhesive agents.

BACKGROUND OF THE INVENTION

The desire to have hair retain a particular shape is widely held. Such style retention is generally accomplished by either of two routes: permanent chemical alteration or temporary alteration of hair style/shape. A temporary alteration is one which can be removed by water or by shampooing. Temporary style alteration has generally been accomplished by means of the application of a composition to dampened hair after shampooing and/or conditioning and prior to drying and/or styling. The materials used to provide setting benefits have generally been resins or gums and have been applied in the form of mousses, gels, lotions, or sprays. This approach presents several significant drawbacks to the user. It requires a separate step following shampooing/conditioning to apply the styling composition. In addition, since the style hold is provided by resin materials which set-up on the hair, the hair tends to feel sticky or stiff after application and it is difficult to restyle the hair without further application of the styling composition.

It has recently been discovered that hair care compositions containing polysiloxane-grafted polymers can provide excellent hair style retention benefits, together with hair conditioning. The compositions may be in any of the conventional forms including, but not limited to, shampoos, conditioners, hair sprays,

- 2 -

tonics, lotions, gels, and mousses. The compositions can provide these benefits to hair without leaving the hair stiff or sticky/tacky feel, as do conventional hair setting ingredients.

5 These types of adhesive, film-forming, polysiloxane-grafted polymers can also be used for other purposes, such as topical application to skin for cosmetic purposes or as a means for delivery of medicaments. The film forming agents can also be used in a wide variety of other adhesive areas, e.g. adhesive paper or binding materials, etc.

10 Polysiloxane-grafted polymers are disclosed for use in EP0 Application 90307528.1, published January 16, 1991 as EP0 Publication 0 408 311 A2, Hayama, et al., U.S. Patent 5,061,481, issued October 29, 1991, Suzuki et al., U.S. Patent 5,106,609, Bolich et al., issued April 21, 1992, U.S. Patent 5,100,658, 15 Bolich et al., issued March 31, 1992, U.S. Patent 5,100,657, Ansher-Jackson, et al., issued March 31, 1992, U.S. Patent 5,104,646, Bolich et al., issued April 14, 1992, U.S. Serial No. 07/758,319, Bolich et al., filed August 27, 1991, and U.S. Serial No. 07/758,320, Torgerson et al., filed August 27, 1991. Adhesive 20 compositions containing film-forming polysiloxane-grafted polymers are also disclosed in U.S. Patent 4,728,571, issued March 1, 1988, Clemens et al., U.S. Patent 5,021,477, issued June 4, 1991, Garbe et al., U.S. Patent 4,981,902, issued January 1, 1991, Garbe et al., U.S. Patent 4,988,506, issued January 29, 1991, Mitra et al., 25 and U.S. Patent 4,981,903, Mitra et al., issued January 1, 1991, Mitra et al.

Whereas excellent performance can be obtained with these polysiloxane-grafted polymers, particularly for hair setting compositions, it remains desirable to achieve improved adhesive 30 performance. It also remains desirable to achieve higher levels of tactile softness for a given level of adhesion for compositions containing these adhesive agents. In particular, for example, it is desirable to provide hair setting compositions with improved hold and/or higher tactile softness for a given level of hold. It

35

- 3 -

is an object of this invention to provide adhesive agents that can provide such enhanced levels of performance.

These and other benefits will become readily apparent from the detailed description which follows.

5 Unless otherwise indicated, all percentages and ratios herein are by weight. The invention hereof can comprise, consist of, or consist essentially of, the essential as well as optional ingredients and components described herein.

SUMMARY OF THE INVENTION

10 The present invention relates to a polymeric adhesive agent, especially a film-forming agent, comprising a polysiloxane-grafted polymer made by the polymerization of polymerizable, polysiloxane containing monomers with polymerizable non-polysiloxane-containing monomers, wherein said adhesive agent has a weight average
15 molecular weight of at least about 20,000, contains from about 1% to about 50%, by weight, of the polysiloxane-containing monomer, and the weight percentage of silicon present as unreacted polysiloxane-containing monomers and polysiloxane-grafted polymers having a viscosity at 25°C of below about 10,000,000 centistokes
20 based on the total silicon present as unreacted polysiloxane-containing monomer and polysiloxane-grafted polymer is about 15% or less. Also, the adhesive agent should contain no more than about 4%, by weight, of unreacted polysiloxane-containing monomer and polysiloxane-grafted polymer having a viscosity at 25°C of below about 10,000,000.
25

In another embodiment, the present invention provides cosmetic compositions, especially hair care compositions, eg. hair setting compositions, comprising the adhesive agent hereof and a carrier suitable for application to the hair.

30 DETAILED DESCRIPTION OF THE INVENTION

The essential, as well as various optional, components of the present invention are described below.

Polymeric Adhesive Agent

The polymeric adhesive agent hereof comprises a film-forming
35 polysiloxane-grafted polymer, made by the polymerization of

- 4 -

polysiloxane-containing monomers with non-polysiloxane-containing monomers such that said adhesive agent has a weight average molecular weight of at least about 20,000, comprises from about 1% to about 50%, by weight, of the polysiloxane-containing monomers, and the weight percentage of unreacted polysiloxane-containing monomers and polysiloxane-grafted polymers having a viscosity at 25°C of below about 10,000,000 centistokes: to total silicon present as unreacted polysiloxane-containing monomer and polysiloxane-grafted polymer is about 15% or less, more preferably about 5% or less. The level of polysiloxane-containing monomers in the adhesive agent, for purposes hereof, includes monomer present in either unreacted (eg., unpolymerized) form as well as monomer incorporated into the adhesive agent in polymer form. Also, the adhesive agent should contain no more than about 4%, by weight, of unreacted polysiloxane-containing monomer and polysiloxane-grafted polymer having a viscosity at 25°C of below about 10,000,000, preferably less than about 3% more preferably less than about 2%, most preferably less than about 1%. The limitation pertaining to the adhesive agent sets forth the maximum viscosity level, as described above, can also be limited to is preferably about 1,000,000, about 100,000 or about 10,000, etc.

Cosmetic compositions of the present invention typically contain from about 0.1% to about 10.0%, preferably from about 0.5% to about 8.0%, of the adhesive agent, although higher or lower amounts may be used for particular applications. The adhesive agent hereof can also be used to advantage in other cosmetic products, such as make-up, mascara and eye-liner, nail polish, etc., as well as topical skin products such as creams and lotions, including for delivery of medicaments or other ingredients to the skin. The adhesive agent hereof can further be used for other adhesive applications, such as adhesive paper and backing paper, etc.

The adhesive agent should have a weight average molecular weight of at least about 20,000. There is no upper limit for molecular weight except that which limits applicability of the

- 5 -

invention for practical reasons, such as processing, aesthetic characteristics, formulateability, etc. In general, the weight average molecular weight will be less than about 10,000,000, more generally less than about 5,000,000, and typically less than about 3,000,000. Preferably, the weight average molecular weight will be between about 50,000 and about 2,000,000, more preferably between about 75,000 and about 1,000,000, most preferably between about 100,000 and about 750,000.

Preferably, especially for cosmetic compositions, the adhesive agents hereof when dried to form a film have a Tg of at least about -20°C, preferably at least about 20°C, so that they are not sticky, or "tacky" to the touch. As used herein, the abbreviation "Tg" refers to the glass transition temperature of the non-silicone backbone, and the abbreviation "Tm" refers to the crystalline melting point of the non-silicone backbone, if such a transition exists for a given polymer. Preferably, the Tm, if any, is also above about -20°C, more preferably above about 20°C.

The polymers useful in the compositions of the present invention are polysiloxane-grafted polymers of polymerizable "silicone-containing", or "polysiloxane-containing", monomers with non-silicone-containing monomers. The polysiloxane-grafted polymers should satisfy the following four criteria:

- (1) when dried the polymer phase-separates into a discontinuous phase which includes the silicone portion and a continuous phase which includes the non-silicone portion;
- (2) the silicone portion is covalently grafted to the non-silicone portion; and
- (3) the molecular weight of the silicone portion is at least about 500; and

When used in a composition, such as a cosmetic composition for application to the hair or skin, the non-silicone portion should render the entire polymer soluble or dispersible in the composition vehicle and permit the polymer to deposit on the intended surface, eg. hair or skin.

- 6 -

The most preferred polymers comprise an organic backbone, especially a carbon backbone such as a vinyl polymeric backbone, and also preferably, a polydimethylsiloxane macromer having a weight average molecular weight of at least about 500, preferably from about 1,000 to about 100,000, more preferably from about 2,000 to about 50,000, most preferably about 5,000 to about 20,000, is grafted to the backbone. Organic backbones contemplated include those that are derived from polymerizable, ethylenically unsaturated monomers. These include vinyl monomers, and other condensation monomers (eg., those that polymerize to form polyamides and polyesters) and ring-opening monomers (eg., ethyl oxazoline and caprolactone). The polymer is such that when it is formulated into the finished composition, when dried, the polymer phase separates into a discontinuous phase which includes the polydimethylsiloxane macromer and a continuous phase which includes the backbone. It is believed that this phase separation property provides a specific orientation of the polymer which results in the desired combination of tactile feel and setting, film-forming, or adhesive benefits. The phase-separating nature of the compositions of the present invention may be determined as follows:

The polymer is cast as a solid film out of a good solvent (i.e., a solvent which dissolves both the backbone and the silicone). This film is then sectioned and examined by transmission electron micrography. Microphase separation is demonstrated by the observation of inclusions in the continuous phase. These inclusions should have the proper size to match the size of the silicone chain (typically a few hundred nm or less) and the proper density to match the amount of silicone present. This behavior is well documented in the literature for polymers with this structure (see, for example, S. D. Smith, Ph.D. Thesis, University of Virginia, 1987, and references cited therein).

A second method for determining phase-separating characteristics involves examining the enrichment of the concentration of silicone at the surface of a polymer film relative to the

- 7 -

concentration in the bulk polymer. Since the silicone prefers the low energy air interface, it preferentially orients on the polymer surface. This produces a surface with the silicone oriented at the surface of the film. This can be demonstrated experimentally by ESCA (electron spectroscopy for chemical analysis) of the dried film surface. Such an analysis shows a high level of silicone and a greatly reduced level of backbone polymer when the film surface is analyzed. (Surface here means the first few tens of Angstroms of film thickness.) By varying the angle of the interrogating beam the surface can be analyzed to varying depths.

Examples of useful polymers and how they are made are described in detail in U.S. Patent 4,693,935, Mazurek, issued September 15, 1987, U.S. Patent 4,728,571, Clemens et al., issued March 1, 1988, both of which are incorporated herein by reference. These polymers are comprised of: at least one free radically polymerizable vinyl monomer or monomers (A); and optionally at least one reinforcing monomer copolymerizable with A which is more hydrophilic than A and is selected from the group consisting of hydrophilic monomers and macromers having a Tg or a Tm above about -20°C (B). The polymers also comprise polysiloxane-containing monomers. (C) Polymerizable macromers which can be used herein shall be referred to herein collectively with polymerizable monomers as "monomers", for convenience. Hydrophobic monomers means monomers which form substantially water insoluble homopolymers. Hydrophilic monomers means monomers which do not form substantially water insoluble homopolymers. Suitable polymers are also disclosed in EPO Application 90307528.1, published as EPO Application 0 408 311 A2 on January 11, 1991, Hayama, et al., U.S. Patent 5,061,481, issued October 29, 1991, Suzuki et al., U.S. Patent 5,106,609, Bolich et al., issued April 21, 1992, U.S. Patent 5,100,658, Bolich et al., issued March 31, 1992, U.S. Patent 5,100,657, Ansher-Jackson, et al., issued March 31, 1992, U.S. Patent 5,104,646, Bolich et al., issued April 14, 1992, U.S. Serial No. 07/758,319, Bolich et al, filed August 27, 1991, and U.S. Serial No. 07/758,320, Torgerson et al., filed

- 8 -

August 27, 1991, all of which are incorporated by reference herein.

5 The polysiloxane-grafted polymers hereof comprise from about 1% to about 50%, by weight of C monomers, i.e., the polysiloxane-containing monomers, and from about 50% to about 99% by weight, of non-polysiloxane-containing monomers, which can be monomers selected from the group consisting of A and B monomers, and mixtures thereof.

10 Representative examples of hydrophobic, A monomers are acrylic or methacrylic acid esters of C_1 - C_{18} alcohols, such as methanol, ethanol, methoxy ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 1-methyl-1-butanol, 3-methyl-1-butanol, 1-methyl-1-pentanol, 2-methyl-1-pentanol, 3-methyl-1-pentanol, 15 t-butanol(2-methyl-2-propanol), cyclohexanol, neodecanol, 2-ethyl-1-butanol, 3-heptanol, benzyl alcohol, 2-octanol, 6-methyl-1-heptanol, 2-ethyl-1-hexanol, 3,5-dimethyl-1-hexanol, 3,5,5-trimethyl-1-hexanol, 1-decanol, 1-dodecanol, 1-hexadecanol, 1-octadecanol, and the like, the alcohols having from about 1-18 carbon atoms with the number of carbon atoms preferably being from about 1-12; styrene; polystyrene macromer; vinyl acetate; vinyl chloride; vinylidene chloride; vinyl propionate; alpha-methylstyrene; t-butylstyrene; butadiene; cyclohexadiene; ethylene; propylene; vinyl toluene; and mixtures thereof. Preferred A monomers include 20 n-butyl methacrylate, isobutyl methacrylate, t-butyl acrylate, t-butyl methacrylate, 2-ethylhexyl methacrylate, methyl methacrylate, and mixtures thereof. Most preferably, A is selected from t-butyl acrylate, t-butyl methacrylate, and mixtures thereof.

30 Representative examples of hydrophilic, B monomers include acrylic acid, methacrylic acid, N,N-dimethylacrylamide, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, methacrylamide, N-t-butyl acrylamide, maleic acid, maleic anhydride and its half esters, crotonic acid, itaconic acid, acrylamide, acrylate alcohols, hydroxyethyl methacrylate, 35 diallyldimethyl ammonium chloride, vinyl pyrrolidone, vinyl ethers

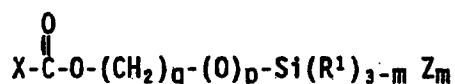
- 9 -

(such as methyl vinyl ether), maleimides, vinyl pyridine, vinyl imidazole, other polar vinyl heterocyclics, styrene sulfonate, allyl alcohol, vinyl alcohol (produced by the hydrolysis of vinyl acetate after polymerization), vinyl caprolactam, and mixtures thereof. Preferred B monomers include acrylic acid, N,N-dimethylacrylamide, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, vinyl pyrrolidone, salts of acids and amines listed above, and mixtures thereof.

The preferred polymerizable polysiloxane-containing monomer (C monomer) can be exemplified by the general formula:



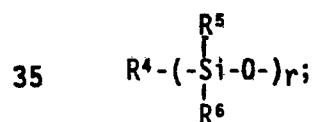
wherein X is a vinyl group copolymerizable with the A and B monomers; Y is a divalent linking group; R is a hydrogen, hydroxyl, lower alkyl (e.g. C₁-C₄), aryl, alkaryl, alkoxy, or alkylamino; Z is a monovalent siloxane polymeric moiety having a number average molecular weight of at least about 500, is essentially unreactive under copolymerization conditions, and is pendant from the vinyl polymeric backbone described above; n is 0 or 1; and m is an integer from 1 to 3. C has a weight average molecular weight as described above. Preferably, the C monomer has a formula selected from the following group:



In this structure, m is 1, 2 or 3 (preferably m = 1); p is 0 or 1; q is an integer from 2 to 6; R¹ is hydrogen, hydroxyl, lower alkyl, alkoxy, alkylamino, aryl, or alkaryl (preferably R⁴ is alkyl); X is



R² is hydrogen or -COOH (preferably R² is hydrogen); R³ is hydrogen, methyl or -CH₂COOH (preferably R³ is methyl); Z is



- 10 -

5 R⁴, R⁵, and R⁶ independently are lower alkyl, alkoxy, alkylamino, aryl, alkaryl, hydrogen or hydroxyl (preferably R⁴, R⁵, and R⁶ are alkyls); and r is an integer of about 5 or higher, preferably about 10 to about 1500 (most preferably r is from about 100 to about 250). Most preferably, R⁴, R⁵, and R⁶ are methyl, p=0, and q=3.

10 In general, the total of A and B monomers in the adhesive agent polymer will preferably be from about 50% to about 99%, more preferably from about 60% to about 98%, most preferably from about 75% to about 95)%, by weight of the polymer of the adhesive agent. The level of A monomers can be from 0% to about 99%; the level of B monomers, from 0% to about 99%; and the level of C monomers, from 1% to about 50%, preferably from about 1% to about 40%, more preferably from about 2% to about 25%, of monomer C. The
15 composition of any particular adhesive agent polymer will help determine its formulational properties. In fact, by appropriate selection and combination of particular A, B and C components, the adhesive agent polymer can be optimized for inclusion in specific vehicles. For example, polymers which are soluble in an aqueous
20 formulation or other polar or hydrophilic solvents preferably have from about 0% to about 85% (preferably from about 5% to about 70%) monomer A, from about 14% to about 95% (preferably from about 29% to about 80%) monomer B, and from about 1% to about 40% (preferably from about 2% to about 25%) monomer C. Polymers which
25 are dispersible in aqueous formulations have the preferred composition: from about 0% to about 70% (preferably from about 5% to about 70%) monomer A, from about 20% to about 80% (preferably from about 20% to about 60%) monomer B, and from about 1% to about 40% (preferably from about 2% to about 25%) monomer C. Polymers
30 which are soluble or dispersible in less polar or nonpolar solvents, such as cyclomethicone, preferably comprise from about 5% to about 98% (preferably from about 50% to about 90%) of monomer A, from 0 to about 80% (preferably from 0% to about 45%, most preferably from 0% to about 20% of monomer B, and from about

35

- 11 -

1% to about 40% (preferably from about 2% to about 25%) of monomer C.

5 The polysiloxane-grafted polymers can be synthesized as follows. In general, the polymers can be made by free radical polymerization of silicone- or polysiloxane-containing monomers with non-silicone- or non-polysiloxane-containing monomers. The
10 filming forming, cosmetic agent comprising this product is prepared by substantially removing the unreacted polysiloxane-containing monomers and polysiloxane-grafted polymers which have a fluid viscosity at 25°C of below about 10,000,000, to the levels defined by silicon present as described above. The monomer and polymeric material removed are both of relatively low molecular weight, compared to the molecular weight of the cosmetic agent hereof.

15 It is not intended to necessarily exclude from this invention any polysiloxane-grafted polymer made by free radical polymerization or by means other than free radical polymerization, so long as the product is substantially free of the above-mentioned, undesired materials, either by means of
20 purification subsequent to reaction or as a result of an improved reaction or different type of synthesis. However, it is to be understood that block copolymers of alternating organic block and silicone blocks are not included as polysiloxane-grafted polymers.

25 The general principles of free radical polymerization methods are well understood. See, for example, Odian, "Principles of Polymerization", 2nd edition, John Wiley & Sons, 1981, pp. 179-318. The desired monomers are all placed in a reactor, along with a sufficient amount of a mutual solvent so that when the reaction is complete the viscosity of the reaction is reasonable.
30 Typical monomer loadings are from about 20% to about 50%. Undesired terminators, especially oxygen, are removed as needed. This is done by evacuation or by purging with an inert gas, such as argon or nitrogen. The initiator is introduced and the reaction brought to the temperature needed for initiation to occur,
35 assuming thermal initiators are used. Alternatively, redox or

- 12 -

radiation initiation can be used as desired. The polymerization is allowed to proceed as long as needed for a high level of conversion to be achieved, typically from a few hours to a few days. The solvent is then removed, usually by evaporation or by precipitating the polymer by addition of a nonsolvent. The polymer is further purified, as needed.

By way of example, Polymers I, II and III, described above, are synthesized in the following manner. There are numerous variations on these procedures which are entirely up to the discretion of the synthetic chemist (e.g., choice of degassing method and gas, choice of initiator type, extent of conversion, reaction loading, etc). The choice of initiator and solvent are often determined by the requirements of the particular monomers used, since different monomers have different solubilities and different reactivities to a specific initiator.

Polymer I: Place 20 parts acrylic acid, 60 parts t-butylacrylate, and 20 parts polysiloxane (10,000 MW)-containing monomer in a flask. Add sufficient ethyl acetate or acetone (preferably acetone) as the reaction solvent to produce a final monomer concentration of 40%. Add initiator, benzoyl peroxide, to a level of 0.5% by weight relative to the amount of monomer. Evacuate the vessel, and refill with nitrogen. Heat to 60°C and maintain this temperature for 48 hours while agitating. Terminate the reaction by cooling to room temperature, and dry off the reaction solvent by pouring the reaction mixture into a teflon-coated pan and placing in a vacuum oven. A similar procedure can be used to make an 80%/120% t-butyl acrylate/polysiloxane (10,000 MW)-containing monomer. Ethyl acetate is the preferred solvent for this synthesis.

Polymer II: Place 20 parts N,N-dimethylacrylamide, 60 parts isobutylmethacrylate, and 20 parts silicone macromer in a reaction vessel fitted with a temperature probe, reflux condenser, inlet port, and argon sparge. Add sufficient toluene to bring the final monomer concentration to 20% by weight. Sparge with argon for 1 to 2 hours. While sparging, heat to 62°C in a water bath. Add

- 13 -

initiator, azobisisobutyronitrile, to a level of 0.25% by weight relative to the weight of monomer present. Maintain temperature at 62°C, with a sufficient rate of argon flow to keep the solution mixed. Monitor the reaction visually, ensuring that no phase separation of reactants occurs during polymerization. If any turbidity is observed, add sufficient warm degassed toluene to eliminate the turbidity. Continue to monitor throughout the reaction. Terminate the reaction after 4 to 6 hours and purify as with Polymer I.

5
10 Polymer III: Place 10.5 parts N,N-dimethylmethacrylamide, 56 parts isobutyl methacrylate, 3.5 parts 2-ethylhexylmethacrylate, and 30 parts 10K PDMS macromer in a reaction vessel fitted with an argon sparge, temperature probe, reflux condenser and inlet port. Add sufficient toluene or isopropanol to bring the final monomer concentration to 20% by weight. Begin stirring and sparge with argon for 1 hour. While sparging, heat to 60°C in a water bath. Add initiator, azobisisobutyronitrile, to a level of 0.25% (if toluene is the solvent) or 0.125% (if isopropanol is the solvent) by weight relative to the weight of monomer present. Continue stirring and a slow argon sparge and maintain the reaction temperature at 60°C. Allow to react for 6 hours. Terminate the reaction and remove the solvent as with Polymer II.

15
20 Removal of unwanted polysiloxane-containing monomer and/or polysiloxane-grafted polymeric material that has viscosity below 10,000,000 at 25°C from free radically polymerized product can be done by any means known in the art. The materials to be removed, in general, will be of lower molecular weight than the average molecular weight of the polymer material prior to extraction. Also, such materials to be removed will contain a relatively high proportion of polysiloxane relative to the organic component-generally, although not necessarily, in excess of 50% polysiloxane.

25
30 Techniques suitable for removing the unwanted material include a variety of standard procedures known in the art.

35

- 14 -

One method that can be used is supercritical fluid extraction, such as with supercritical carbon dioxide.

Supercritical fluid extraction is carried out on polymer which has been dried from the original reaction mixture to remove excess reaction solvent. Dried polymer is preferably ground to create a fine powder, which allows for increased surface area and maximum extraction efficiency. Extraction can be carried out using supercritical carbon dioxide in conventional extractors suitable for supercritical fluid extraction. The extraction should be conducted at a temperature of at least about 40 deg C and a pressure of between about 400-600 atmospheres. The particular temperature and pressure will depend upon criteria well known in the art, such as specific solvent, polymer sample size, fineness of the ground material, and the desired extraction efficiency. Extraction occurs via continuous purging under pressure with supercritical carbon dioxide, typically over a period of about 1-4 hours. Unreacted polysiloxane-containing monomer and low molecular weight polysiloxane-containing polymer is solubilized by carbon dioxide and is then transported away from the remaining polymer via standard procedures, e.g., by a transfer line.

Another generally applicable method is membrane separation, performed in accordance with standard techniques known in the art.

A method which can be useful, particularly for adhesive agents utilizing polysiloxane-grafted polymers that are soluble in water, alcohol, or other polar solvents, is solvent extraction with a nonpolar solvent. Suitable solvents include C_3 - C_8 hydrocarbons, preferably C_5 - C_6 hydrocarbons, such as hexane. Before performing the extraction, the polymer reaction product is precipitated out of the reaction solvent (e.g., with water), and dried. The extraction solvent is preferably heated to near or slightly above the average Tg of the non-silicone backbone portion of the polysiloxane-grafted polymer of the adhesive agent. The temperature should be high enough so that the polymer softens, but not so high such that it congeals. The Tg of the polymer will

- 15 -

5 vary from species to species of polymer. The extraction solvent and reaction product can be mixed before, or after heating the solvent. The extraction solvent and polymer reaction product should be held with mixing and preferably in an excess of solvent, for a reasonable period to effectuate removal of the soluble materials. This period will depend upon the reflux temperature of the solvent, the Tg of the polysiloxane-grafted polymer of the adhesive agent, the temperature to which the solvent is actually heated, the desired level of removal of unreacted monomer and the polysiloxane-containing polymer having viscosity at 25°C below about 10,000,000, and the number of cycles of solvent extraction to be performed. Typically, the solvent extraction periods will be from about one-half hour to about two hours, more typically from about one-half hour to about one hour. The solvent can be removed after each cycle by conventional means, e.g., decanting, filtering, etc., with drying or distillation to remove trace extraction solvent remaining in the product after the final extraction cycle.

10 Analysis of the polymer reaction product and the extracted materials, and the purified film-forming agent can be done by conventional analysis techniques known in the art. These include, for example, nuclear magnetic resource (NMR), infrared molecular spectroscopies, gel permeation/size exclusion chromatography, and atomic absorption and emission spectroscopies.

25

Carrier

The cosmetic compositions of the invention comprise the a carrier, or a mixture of such carriers, which are suitable for application to skin or hair. The carriers are present at from about 0.5% to about 99.5%, preferably from about 5.0% to about 99.5%; most preferably from about 10.0% to about 98.0%, of the composition. As used herein, the phrase "suitable for application to hair" means that the carrier does not damage or negatively affect the aesthetics of hair or cause irritation to skin. Choice of appropriate solvent will also depend on the particular polymer

30

35

- 16 -

to be used, and whether the product formulated is meant to be left on the surface to which it is applied (e.g., hair spray, mousse, tonic) or rinsed off (e.g., shampoo, conditioner) after use.

5 The carriers used herein include solvents, as well as other carrier or vehicle components conventionally used in hair care compositions. The solvent selected must be able to dissolve or disperse the particular silicone-grafted polymer being used. The
10 silicone-grafted polymers can be designed, by appropriate combination of monomers, for formulation with a wide range of solvents. Suitable solvents for use in the present invention include, but are not limited to, water, lower alcohols (e.g. C₁-C₆ monohydric alcohols, such as ethanol and isopropanol), hydro-
15 alcoholic mixtures, hydrocarbons (such as isobutane, hexane, decene, acetone), halogenated hydrocarbons (such as Freon), linalool, hydrocarbon esters (such as ethyl acetate, dibutyl phthalate), volatile silicon derivatives, especially siloxanes (such as phenyl pentamethyl disiloxane, methoxypropyl heptamethyl cyclo-
20 tetrasiloxane, chloropropyl pentamethyl disiloxane, hydroxypropyl pentamethyl disiloxane, octamethyl cyclotetrasiloxane, decamethyl cyclopentasiloxane, cyclomethicone, and dimethicone (having for example, viscosity at 25°C of about 15 centipoise or less), and mixtures thereof. Preferred solvents include water, ethanol, volatile silicone derivatives, and mixtures thereof. The solvents
25 used in such mixtures may be miscible or immiscible with each other.

Where the cosmetic compositions are conditioner compositions, such as hair rinses or skin conditioners the carrier may include gel vehicle materials. This gel vehicle comprises two essential components: a lipid vehicle material and a cationic surfactant
30 vehicle material. Cationic surfactant materials are described in detail below. Gel-type vehicles are generally described in the following documents, all incorporated by reference herein: Barry, "The Self Bodying Action of the Mixed Emulsifier Sodium Dodecyl Sulfate/Cetyl Alcohol", 28 J. of Colloid and Interface Science
35 82-91 (1968); Barry, et al., "The Self-Bodying Action of

- 17 -

Alkyltrimethylammonium Bromides/Cetostearyl Alcohol Mixed Emulsifiers; Influence of Quaternary Chain Length", 35 J. of Colloid and Interface Science 689-708 (1971); and Barry, et al., "Rheology of Systems Containing Cetomacrogol 1000 - Cetostearyl Alcohol, I. Self Bodying Action", 38 J. of Colloid and Interface Science 616-625 (1972).

The carrier may incorporate one or more lipid vehicle materials which are essentially water-insoluble, and contain hydrophobic and hydrophilic moieties. Lipid vehicle materials include naturally or synthetically-derived acids, acid derivatives, alcohols, esters, ethers, ketones, and amides with carbon chains of from about 12 to about 22, preferably from about 16 to about 18, carbon atoms in length. Fatty alcohols and fatty esters are preferred; fatty alcohols are particularly preferred.

Lipid vehicle materials among those useful herein are disclosed in Bailey's Industrial Oil and Fat Products, (3rd edition, D. Swern, ed., 1979), incorporated by reference herein. Fatty alcohols included among those useful herein are disclosed in the following documents, all incorporated by reference herein: U.S. Patent 3,155,591, Hilfer, issued November 3, 1964; U.S. Patent 4,165,369, Watanabe, et al., issued August 21, 1979; U.S. Patent 4,269,824, Villamarin, et al., issued May 26, 1981; British Specification 1,532,585, published November 15, 1978; and Fukushima, et al., "The Effect of Cetostearyl Alcohol in Cosmetic Emulsions", 98 Cosmetics & Toiletries 89-112 (1983). Fatty esters included among those useful herein are disclosed in U.S. Patent 3,341,465, Kaufman, et al., issued September 12, 1976 (incorporated by reference herein). If included in the compositions of the present invention, the lipid vehicle material is present at from about 0.1% to about 10.0% of the composition; the cationic surfactant vehicle material is present at from about 0.05% to about 5.0% of the composition.

Preferred esters for use herein include cetyl palmitate and glycerylmonostearate. Cetyl alcohol and stearyl alcohol are preferred alcohols. A particularly preferred lipid vehicle

- 18 -

material is comprised of a mixture of cetyl alcohol and stearyl alcohol containing from about 55% to about 65% (by weight of mixture) of cetyl alcohol.

5 Preferred carrier for use in the compositions of the present invention, especially for hair rinses, include combinations of hydrophobically-modified hydroxyethyl cellulose materials with thickeners (such as locust bean gum), particular surfactants, quaternary ammonium compounds (such as ditallowdimethyl ammonium chloride), and/or chelating agents (such as EDTA). These vehicles
10 are described in detail in the following patents: U.S. Patent 5,106,609, issued April 21, 1992 to Bolich et al., U.S. Patent 5,100,658, issued March 31, 1992 to Bolich et al., U.S. Patent 5,104,646, issued April 14, 1992 to Bolich et al., and U.S. Patent 5,100,657, issued March 31, 1992 to Ansher-Jackson et al., each
15 incorporated herein by reference.

Carriers, suitable for use with the present invention include, for example, those used in the formulation of tonics, mousses, gels and hair sprays. Tonics, gels and non-aerosol hair sprays utilize a solvent such as water or alcohol while mousses
20 and aerosol hair sprays additionally utilize a propellant such as trichlorofluoromethane, dichlorodifluoromethane, difluoroethane, dimethylether, propane, n-butane or isobutane. A tonic or hair spray product having a low viscosity may also utilize an emulsifying agent. Examples of suitable emulsifying agents include
25 nonionic, cationic, anionic surfactants, or mixtures thereof. Fluorosurfactants are especially preferred, particularly if the product is a hair spray composition and most especially if it is a spray composition having relatively low levels of volatile organic solvents, such as alcohols, and relatively high levels of water
30 (e.g., in excess of about 10%, by weight water). If such an emulsifying agent is used, it is preferably present at a level of from about 0.01% to about 7.5% of the composition. The level of propellant can be adjusted as desired but is generally from about 3% to about 30% of mousse compositions and from about 15% to about
35 50% of the aerosol hair spray compositions.

- 19 -

Suitable spray containers are well known in the art and include conventional, non-aerosol pump sprays i.e., "atomizers," aerosol containers or can having propellant, as described above, and also pump aerosol containers utilizing compressed air as the propellant. Pump aerosol containers are disclosed, for example, in U.S. Patents 4,077,441, March 7, 1978, Olofsson and 4,850,577, July 25, 1989, TerSteege, both incorporated by reference herein, and also in U.S. Serial No. 07/839,648, Gosselin, Lund, Sojka, and Lefebvre, filed February 21, 1992, "Consumer Product Package Incorporating A Spray Device Utilizing Large Diameter Bubbles. Pump aerosols hair sprays using compressed air are also currently marketed by The Procter & Gamble Company under their tradename VIDAL SASSOON AIRSPRAY® hair sprays.

Optional Ingredients

The cosmetic compositions of the present invention may be formulated in a wide variety of product types, including mousses, gels, lotions, tonics, sprays, shampoos and conditioners. The additional components required to formulate such products vary with product type and can be routinely chosen by one skilled in the hair care product art. The following is a description of some of these additional components.

Surfactants

Surfactants are preferred optional ingredients in the compositions of the invention, particularly shampoo and conditioner compositions. When present, the surfactant comprises from about 0.05% to about 50% of the composition. For a shampoo, the level is preferably from about 10% to about 30%, most preferably from about 12% to about 25%, of the composition. For conditioners, the preferred level of surfactant is from about 0.2% to about 3%. Surfactants useful in compositions of the present invention include anionic, nonionic, cationic, zwitterionic and amphoteric surfactants.

Synthetic anionic detergents useful herein, particularly for shampoo compositions, include alkyl and alkyl ether sulfates. These materials typically have the respective formulae ROS_3M and

- 20 -

$RO(C_2H_4O)_xSO_3M$, wherein R is alkyl or alkenyl of from about 10 to about 20 carbon atoms, x is 1 to 10, and M is a water-soluble cation such as ammonium, sodium, potassium and triethanolamine.

Another suitable class of anionic surfactants are the water-soluble salts of the organic, sulfuric acid reaction products of the general formula:



wherein R_1 is chosen from the group consisting of a straight or branched chain, saturated aliphatic hydrocarbon radical having from about 8 to about 24, preferably about 12 to about 18, carbon atoms; and M is a cation. Important examples are the salts of an organic sulfuric acid reaction product of a hydrocarbon of the methane series, including iso-, neo-, and n-paraffins, having about 8 to about 24 carbon atoms, preferably about 12 to about 18 carbon atoms and a sulfonating agent, e.g., SO_3 , H_2SO_4 , oleum, obtained according to known sulfonation methods, including bleaching and hydrolysis. Preferred are alkali metal and ammonium sulfonated C_{12-18} n-paraffins.

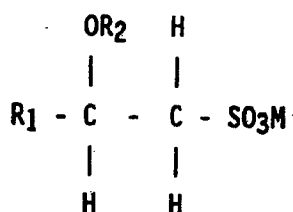
Additional examples of anionic synthetic surfactants which come within the terms of the present invention are the reaction products of fatty acids esterified with isethionic acid and neutralized with sodium hydroxide where, for example, the fatty acids are derived from coconut oil; sodium or potassium salts of fatty acid amides of methyl tauride in which the fatty acids, for example, are derived from coconut oil. Other anionic synthetic surfactants of this variety are set forth in U.S. Patents 2,486,921; 2,486,922; and 2,396,278.

Still other anionic synthetic surfactants include the class designated as succinamates. This class includes such surface active agents as disodium N-octadecylsulfosuccinamate; tetrasodium N-(1,2-dicarboxyethyl)-N-octadecylsulfosuccinamate; diamyl ester of sodium sulfosuccinic acid; dihexyl ester of sodium sulfosuccinic acid; dioctyl esters of sodium sulfosuccinic acid.

Other suitable anionic surfactants utilizable herein are olefin sulfonates having about 12 to about 24 carbon atoms. The

- 21 -

term "olefin sulfonates" is used herein to mean compounds which can be produced by the sulfonation of α -olefins by means of uncomplexed sulfur trioxide, followed by neutralization of the acid reaction mixture in conditions such that any sulfones which have been formed in the reaction are hydrolyzed to give the corresponding hydroxy-alkanesulfonates. The α -olefins from which the olefin sulfonates are derived are mono-olefins having about 12 to about 24 carbon atoms, preferably about 14 to about 16 carbon atoms. Another class of anionic organic surfactants are the β -alkyloxy alkane sulfonates. These compounds have the following formula:



where R_1 is a straight chain alkyl group having from about 6 to about 20 carbon atoms, R_2 is a lower alkyl group having from about 1 (preferred) to about 3 carbon atoms, and M is a water-soluble cation as hereinbefore described.

Many additional nonsoap synthetic anionic surfactants are described in McCutcheon's, Detergents and Emulsifiers, 1984 Annual, published by Allured Publishing Corporation, which is incorporated herein by reference. Also U.S. Patent 3,929,678, Laughlin et al., issued December 30, 1975, discloses many other anionic as well as other surfactant types and is incorporated herein by reference.

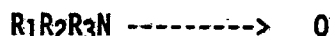
Nonionic surfactants, which are preferably used in combination with an anionic, amphoteric or zwitterionic surfactant, can be broadly defined as compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. Examples of preferred classes of nonionic surfactants are:

- 22 -

2. Those derived from the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine products.

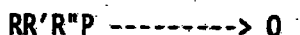
5 3. The condensation product of aliphatic alcohols having from about 8 to about 18 carbon atoms, in either straight chain or branched chain configuration, with ethylene oxide, e.g., a coconut alcohol ethylene oxide condensate having from about 10 to about 30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from about 10 to about 14 carbon atoms.

10 4. Long chain tertiary amine oxides such as those corresponding to the following general formula:



wherein R_1 contains an alkyl, alkenyl or monohydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties, and from 0 to about 1 glyceryl moiety, 15 and R_2 and R_3 contain from about 1 to about 3 carbon atoms and from 0 to about 1 hydroxy group, e.g., methyl, ethyl, propyl, hydroxyethyl, or hydroxypropyl radicals (the arrow in the formula is a conventional representation of a semipolar bond).

20 5. Long chain tertiary phosphine oxides corresponding to the following general formula:



wherein R contains an alkyl, alkenyl or monohydroxyalkyl radical ranging from about 8 to about 18 carbon atoms in chain length, 25 from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety and R' and R'' are each alkyl or monohydroxyalkyl groups containing from about 1 to about 3 carbon atoms. The arrow in the formula is a conventional representation of a semipolar bond.

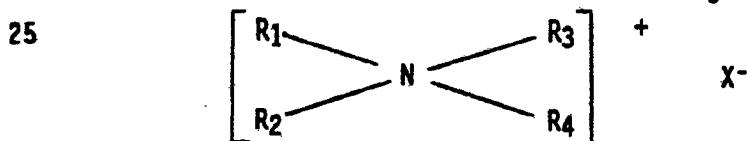
30 6. Long chain dialkyl sulfoxides containing one short chain alkyl or hydroxy alkyl radical of from about 1 to about 3 carbon atoms (usually methyl) and one long hydrophobic chain which include alkyl, alkenyl, hydroxy alkyl, or keto alkyl radicals containing from about 8 to about 20 carbon atoms, from 0 to about 35 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety.

- 23 -

Examples include: octadecyl methyl sulfoxide, 2-ketotridecyl methyl sulfoxide, 3,6,9,-trioctadecyl 2-hydroxyethyl sulfoxide, dodecyl methyl sulfoxide, oleyl 3-hydroxypropyl sulfoxide, tetradecyl methyl sulfoxide, 3-methoxytridecyl methyl sulfoxide, 3-hydroxytridecyl methyl sulfoxide, 3-hydroxy-4-dodecoxybutyl methyl sulfoxide.

Cationic surfactants useful in compositions of the present invention, particularly the conditioner compositions, contain amino or quaternary ammonium hydrophilic moieties which are positively charged when dissolved in the aqueous composition of the present invention. Cationic surfactants among those useful herein are disclosed in the following documents, all incorporated by reference herein: M.C. Publishing Co., McCutcheon's, Detergents & Emulsifiers, (North American edition 1979); Schwartz, et al., Surface Active Agents, Their Chemistry and Technology, New York: Interscience Publishers, 1949; U.S. Patent 3,155,591, Hilfer, issued November 3, 1964; U.S. Patent 3,929,678, Laughlin, et al., issued December 30, 1975; U.S. Patent 3,959,461, Bailey, et al., issued May 25, 1976; and U.S. Patent 4,387,090, Bolich, Jr., issued June 7, 1983. If included in the compositions of the present invention, the cationic surfactant is present at from about 0.05% to about 5%.

Among the quaternary ammonium-containing cationic surfactant materials useful herein are those of the general formula:



wherein R_1 - R_4 are independently an aliphatic group of from about 1 to about 22 carbon atoms, or an aromatic, alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, aryl or alkylaryl group having from about 12 to about 22 carbon atoms; and X is an anion selected from halogen, acetate, phosphate, nitrate and alkylsulfate radicals. The aliphatic groups may contain, in addition to carbon and hydrogen atoms, ether linkages, and other groups such as amino

- 24 -

groups. The longer chain aliphatic groups, eg., those of about 12 carbons, or higher, can be saturated or unsaturated.

Other quaternary ammonium salts useful herein are diquaternary ammonium salts, such as tallow propane diammonium dichloride.

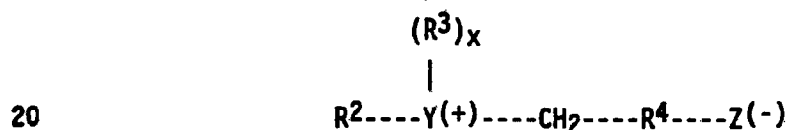
Quaternary ammonium salts include dialkyldimethyl-ammonium chlorides, wherein the alkyl groups have from about 12 to about 22 carbon atoms and are derived from long-chain fatty acids, such as hydrogenated tallow fatty acid (tallow fatty acids yield quaternary compounds wherein R₁ and R₂ have predominately from 16 to 18 carbon atoms). Examples of quaternary ammonium salts useful in the present invention include ditallowdimethyl ammonium chloride, ditallowdimethyl ammonium methyl sulfate, dihexadecyl dimethyl ammonium chloride, di(hydrogenated tallow) dimethyl ammonium chloride, dioctadecyl dimethyl ammonium chloride, dieicosyl dimethyl ammonium chloride, didocosyl dimethyl ammonium chloride, di(hydrogenated tallow) dimethyl ammonium acetate, dihexadecyl dimethyl ammonium chloride, dihexadecyl dimethyl ammonium acetate, ditallow dipropyl ammonium phosphate, ditallow dimethyl ammonium nitrate, di(coconutalkyl) dimethyl ammonium chloride, and stearyl dimethyl benzyl ammonium chloride. Ditallow dimethyl ammonium chloride, dicetyl dimethyl ammonium chloride, stearyl dimethyl benzyl ammonium chloride and cetyl trimethyl ammonium chloride are preferred quaternary ammonium salts useful herein. Di-(saturated or unsaturated tallow) dimethyl ammonium chloride is a particularly preferred quaternary ammonium salt.

Salts of primary, secondary and tertiary fatty amines are also suitable cationic surfactant materials. The alkyl groups of such amines preferably have from about 12 to about 22 carbon atoms, and may be substituted or unsubstituted. Such amines, useful herein, include stearamido propyl dimethyl amine, diethyl amino ethyl stearamide, dimethyl stearamine, dimethyl soyamine, soyamine, myristyl amine, tridecyl amine, ethyl stearylamine, N-tallowpropane diamine, ethoxylated (5 moles E.O.) stearylamine, dihydroxy ethyl stearylamine, and arachidylbehenylamine. Suitable

- 25 -

amine salts include the halogen, acetate, phosphate, nitrate, citrate, lactate and alkyl sulfate salts. Such salts include stearylamine hydrochloride, soyamine chloride, stearylamine formate, N-tallowpropane diamine dichloride and stearamidopropyl dimethylamine citrate. Cationic amine surfactants included among those useful in the present invention are disclosed in U.S. Patent 4,275,055; Nachtigal, et al., issued June 23, 1981, incorporated by reference herein.

Zwitterionic surfactants, useful in shampoos as well as conditioners, are exemplified by those which can be broadly described as derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium compounds, in which the aliphatic radicals can be straight or branched chain, and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water-solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. A general formula for these compounds is:



wherein R^2 contains an alkyl, alkenyl, or hydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety; Y is selected from the group consisting of nitrogen, phosphorus, and sulfur atoms; R^3 is an alkyl or monohydroxyalkyl group containing about 1 to about 3 carbon atoms; X is 1 when Y is a sulfur atom, and 2 when Y is a nitrogen or phosphorus atom; R^4 is an alkylene or hydroxyalkylene of from about 1 to about 4 carbon atoms and Z is a radical selected from the group consisting of carboxylate, sulfonate, sulfate, phosphonate, and phosphate groups.

Other zwitterionics such as betaines are also useful in the present invention. Examples of betaines useful herein include the high alkyl betaines, such as coco dimethyl carboxymethyl betaine, lauryl dimethyl carboxymethyl betaine, lauryl dimethyl alpha-carboxyethyl betaine, cetyl dimethyl carboxymethyl betaine, lauryl

- 26 -

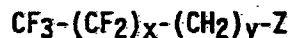
bis-(2-hydroxyethyl) carboxymethyl betaine, stearyl bis-(2-hydroxypropyl) carboxymethyl betaine, oleyl dimethyl gamma-carboxypropyl betaine, and lauryl bis-(2-hydroxypropyl)alpha-carboxyethyl betaine. The sulfobetaines may be represented by
5 coco dimethyl sulfopropyl betaine, stearyl dimethyl sulfopropyl betaine, lauryl dimethyl sulfoethyl betaine, lauryl bis-(2-hydroxyethyl) sulfopropyl betaine and the like; amidobetaines and amidosulfobetaines, wherein the $\text{RCONH}(\text{CH}_2)_3$ radical is attached to the nitrogen atom of the betaine are also useful in this
10 invention.

Examples of amphoteric surfactants which can be used in the compositions of the present invention are those which are broadly described as derivatives of aliphatic secondary and tertiary amines in which the aliphatic radical can be straight or branched
15 chain and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. Examples of compounds falling within this definition are sodium 3-dodecyl-aminopropionate, sodium 3-dodecylamino-
20 propane sulfonate, N-alkyltaurines such as the one prepared by reacting dodecylamine with sodium isethionate according to the teaching of U.S. Patent 2,658,072, N-higher alkyl aspartic acids such as those produced according to the teaching of U.S. Patent 2,438,091, and the products sold under the trade name "Miranol" and described in U.S. Patent 2,528,378.
25

Fluorosurfactant

The compositions of the present invention can contain, fluorosurfactant. Suitable fluorosurfactant can be cationic, anionic, amphoteric, zwitterionic, nonionic or a mixture thereof.

30 Fluorosurfactants include perfluorinated compounds such as those represented by the formula



where Z is a water solubilizing group of either organic or inorganic character, x is an integer which is generally from 2 to
35 17, particularly from 7 to 11, and y is an integer from 0 to 4,

- 27 -

and said compounds may be cationic, anionic, amphoteric or zwitterionic, depending upon the nature of the grouping or groupings encompassed by Z. The Z groups may be or may comprise sulfate, sulfonate, carboxylate, amine salt, quaternary ammonium, phosphate, phosphonate, and combinations thereof. The perfluorinated compounds are known in the art. These compounds are described in U.S. Patent 4,176,176, Cella et al., issued November 27, 1979; U.S. Patent 3,993,745, Cella et al., issued November 23, 1976, and U.S. Patent 3,993,744, Cella et al., issued November 23, 1976, each being incorporated herein by reference.

Cationic fluorosurfactants include fluorinated alkyl quaternary ammonium salts having a variety of anionic counterions, including iodide, chloride, methosulfate, phosphate, and nitrate salts, preferably an iodide; and those fluorosurfactants conforming to the formula $R_fCH_2CH_2SCH_2CH_2N^+(CH_3)_3[CH_3SO_4]^-$ wherein $R_f = F(CF_2CF_2)_{3-8}$, such as Zonyl FSC[®] supplied by DuPont. Preferred fluorinated alkyl quaternary ammonium iodides are supplied under the tradename Fluorad FC-135[®] supplied by 3M.

Anionic fluorosurfactants include mono-, and bis-perfluoroalkyl phosphates, such as Zonyl FSP[®] supplied by DuPont and conforming to the general formulae $(R_fCH_2CH_2O)P(O)(ONH_4)_2$ and $(R_fCH_2CH_2O)_2P(O)(ONH_4)$ wherein $R_f = F(CF_2CF_2)_{3-8}$; mono- and bis-fluoroalkyl phosphates, having a variety of cationic counterions such as ammonium, sodium, potassium, triethanolamine and diethanolamine salts, preferably ammonium salts, complexed with non-fluorinated quats, preferably aliphatic quaternary methosulfates, such as Zonyl FSJ[®] supplied by DuPont; perfluoroalkyl sulfonic acid having a variety of cationic counterions such as ammonium, sodium, potassium, triethanolamine and diethanolamine salts, preferably ammonium salts, such as Zonyl TBS[®] supplied by DuPont and conforming to the formula $R_fCH_2CH_2SO_3X$ wherein $R_f = F(CF_2CF_2)_{3-8}$ and $X = H$ and NH_4 ; telomer phosphates, having a variety of cationic counterions such as ammonium, sodium, potassium, triethanolamine and diethanolamine salts, preferably diethanolamine salts, such as Zonyl RP[®] supplied by DuPont; amine

- 28 -

perfluoroalkyl sulfonates, such as Fluorad FC-99[®] supplied by 3M; ammonium perfluoroalkyl sulfonates, such as Fluorad FC-93[®], Fluorad FC-120[®] and L-12402[®], supplied by 3M; potassium perfluoroalkyl sulfonates, such as Fluorad FC-95[®] and Fluorad FC-98[®] supplied by 3M; potassium fluorinated alkyl carboxylates, such as Fluorad FC-129[®] supplied by 3M; ammonium perfluoroalkyl carboxylates, such as Fluorad FC-143[®] supplied by 3M; and those fluorosurfactants conforming to the general formula $R_fCH_2CH_2SCH_2CH_2CO_2Li$ wherein $R_f=F(CF_2CF_2)_{3-8}$, such as Zonyl FSA[®] supplied by DuPont.

Amphoteric fluorosurfactants include fluorinated alkyl amphoterics such as Fluorad FC-100[®] supplied by 3M.

Zwitterionic fluorosurfactants preferred for use in the present compositions are those fluorosurfactants conforming to the formula $R_fCH_2CH(OCOCH_3)CH_2N^+(CH_3)_2CH_2CO_2^-$ wherein $R_f=F(CF_2CF_2)_{3-8}$ such as Zonyl FSK[®] supplied by DuPont.

Fluorosurfactants can be used alone or in combination in the hair spray compositions of the present invention.

Fluorosurfactants, when used, will typically be present at from about 0.01% to about 2%, preferably from about 0.01% to about 1.5%, by weight of the composition.

The above-mentioned surfactants can be used alone or in combination in the compositions hereof.

The cosmetic compositions herein can contain a variety of other optional components suitable for rendering such compositions more cosmetically or aesthetically acceptable or to provide them with additional usage benefits. Such conventional optional ingredients are well-known to those skilled in the art, e.g., pearlescent aids, such as ethylene glycol distearate; preservatives, such as benzyl alcohol, methyl paraben, propyl paraben and imidazolidinyl urea; thickeners and viscosity modifiers, such as a diethanolamide of a long chain fatty acid (e.g., PEG 3 lauric diethanolamide), cocomonooethanol amide, dimethicone copolyols, guar gum, methyl cellulose, starches and starch derivatives; fatty alcohols, such as cetearyl alcohol; sodium chloride; sodium

- 29 -

sulfate; polyvinyl alcohol; ethyl alcohol; pH adjusting agents, such as citric acid, sodium citrate, succinic acid, phosphoric acid, sodium hydroxide, sodium carbonate; salts, in general, such as potassium acetate and sodium chloride; coloring agents, such as any of the FD&C or D&C dyes; hair oxidizing (bleaching) agents, such as hydrogen peroxide, perborate and persulfate salts; hair reducing agents, such as the thioglycolates; perfumes; sequestering agents, such as disodium ethylenediamine tetra-acetate; and polymer plasticizing agents, such as glycerin, disobutyl adipate, butyl stearate, and propylene glycol. Such optional ingredients generally are used individually at levels of from about 0.01% to about 10.0%, preferably from about 0.05% to about 5.0%, of the composition.

The pH of the present compositions generally will be between about 3 and about 9, preferably between about 4 and about 8.

As with all compositions, the present invention should not contain components which unduly interfere with the performance of the compositions.

The cosmetic compositions of the present invention can be made using conventional formulation and mixing techniques. Methods of making various types of cosmetic compositions are described more specifically in the following examples.

Method of Use

The cosmetic compositions of the present invention are used in conventional ways to provide the conditioning/styling/hold/adhesive/film-forming or other benefits of the present invention. Such method of use depends upon the type of composition employed but generally involves application of an effective amount of the product to the hair or skin, which may then be rinsed from the hair or skin (as in the case of shampoos and some conditioning products) or allowed to remain on the hair (as in the case of spray, mousse, gel, skin lotion, film-forming skin lotion with medicament, and tonic products). By "effective amount" is meant an amount sufficient to provide the film-forming benefits desired. Preferably, hair rinse, mousse, and gel

- 30 -

products are applied to wet or damp hair prior to drying and styling of the hair. After such compositions are applied to the hair, the hair is dried and styled in the usual ways of the user. Hair sprays are typically applied to dry hair after it has already been dried and styled. Cosmetics and skin lotions are applied to face, skin, or eye area in the conventional manners of usage for those types of products.

In another aspect hereof, adhesive agents containing polysiloxane-grafted polymers, such as those described in U.S. Patent 4,693,935, Mazurek, issued September 15, 1987 and U.S. Patent 4,728,571, Clemens et al., issued March 1, 1988, can be used in adhesive products such as adhesive tapes and backing sheets for adhesive materials. Thus, the adhesive agents hereof also can include non-pressure sensitive as well as pressure sensitive film-forming polymers.

The following experimentals and examples further illustrate preferred embodiments within the scope of the present invention. The examples are given solely for the purposes of illustration and are not to be construed as limitations of the present invention as many variations of the invention are possible without departing from its spirit and scope.

Experimental A

A 60%/20%/20% t-butyl acrylate/acrylic acid/polydimethylsiloxane-containing (PDMS) vinyl monomer (10,000 MW) is made by free radical polymerization in an acetone reaction medium, as described above for Polymer I. The percentages represent the weight percent of the total monomer added to the reaction.

The reaction product is precipitated out of the acetone by water addition and dried. Hexane extraction of the reaction product is then performed by adding an excess of hexane to the reaction product and heating to reflux, about 70°C. The Tg of the non-silicone portion of the adhesive agent polymer is about 63°C. The mixture is held at this temperature with stirring for about 30 minutes and cooled to room temperature. The hexane is removed by vacuum suction. Two more hexane extraction cycles are conducted

- 31 -

in the same manner as above. After the third cycle, residual hexane remaining with the product is removed by distillation and vacuum drying.

Experimental B

5 An 80%/20% t-butyl acrylate PDMS (10,000 MW) polymer is made according to the same procedures as for Polymer I, above, except that the monomers that are polymerized are 80%, by weight, t-butyl acrylate and 20%, by weight, of the PDMS-containing vinyl monomer. The reaction medium is ethyl acetate.

10 The reaction product is precipitated out of the reaction solvent by water addition and dried. The polymer is next ground to a fine powder in preparation for supercritical fluid extraction with carbon dioxide. The extraction is carried out at a temperature of about 40°C and a pressure of about 600 atmospheres. 15 The extraction vessel is continuously purged under pressure with supercritical carbon dioxide over a period of about 1 hour.

Low molecular weight polysiloxane-containing monomer and polymer about 1 hour is solubilized by the supercritical carbon dioxide and transported away from the remaining polymer via a 20 transfer line, which is maintained at identical temperature and pressure as the extraction vessel. The extracted materials are collected in an extraction vessel. Following extraction, the system is depressurized and dry, extracted polymer is recovered from the extraction vessel.

25 EXAMPLES I-III

The following are hair spray compositions representative of the present invention.

	<u>Component</u>	<u>Example # (Weight %)</u>		
		<u>I</u>	<u>II</u>	<u>III</u>
30	Polysiloxane-Grafted Polymer (Exp. A)	4.5	4.5	4.5
	Ethanol	79.0	79.0	86.4
	Diisobutyl adipate	0.7	--	--
	Potassium Hydroxide Solution (45% conc)	1.0	1.0	1.0
	Perfume	0.2	0.2	0.2
	FC-120 Fluorosurfactant (3M Co)(25% active)	--	--	0.14
	Water	q.s. to 100%		

35 This product is prepared by dissolving the silicone polymer to the ethanol and mixing for several hours until all the polymer

- 32 -

is dissolved. Plasticizer is then added, if applicable. Potassium hydroxide is then added. Water or water/surfactant, as applicable, is added. Fragrance is added last. All ingredients are added under mixing conditions. The product can be packaged in conventional nonaerosol pump spray containers and compressed air pump spray aerosol containers.

EXAMPLE IV

The following is a hair grooming tonic composition representative of the present invention.

Component	Weight %
Polysiloxane-Grafted Polymer (Exp. A)	0.70
Perfume	0.10
Ethanol	q.s.

The composition is made by mixing the above components together in a conventional manner.

EXAMPLE V

The following is a shampoo composition representative of the present invention.

Component	Weight %
Ammonium laureth sulfate	7.00
Cocamido propyl betaine	6.00
Polysiloxane-Grafted Polymer (Exp. A)	2.00
Ethanol	10.00
PEG 150 distearate	2.00
NaOH	0.15
Glydant ¹	0.38
Perfume	1.00
DRO H ₂ O	q.s.

¹ preservative commercially available from Glyco, Inc.

The shampoo is prepared by combining the ammonium laureth sulfate (normally supplied as a 28% solution in water) and Silicone Copolymer and heating to 70°C for about 1/2 hour with mixing. The remaining ingredients are added and mixed for an additional 1/2 hour. The batch is then cooled to ambient

- 33 -

temperature. Composition pH is adjusted to 6.5 by the addition of citric acid or sodium hydroxide, if necessary.

EXAMPLE VI

5 The following is a cold-wave hair perm composition representative of the present invention.

	<u>Component</u>	<u>Weight %</u>
	Thioglycolic acid	5.00
	Monoethanolamine	6.00
	Polysiloxane-Grafted Polymer (Exp. A)	1.50
10	PEG 10 monostearate	0.50
	DRO H ₂ O	q.s.

The composition is prepared by blending all the ingredients with agitation for about 1/2 hour at 60°C and then cooling to ambient temperature.

15

EXAMPLE VII

The following is a styling gel composition representative of the present invention.

	<u>Component</u>	<u>Weight %</u>
	Polysiloxane-Grafted Polymer (Exp. A)	2.00
20	Carbopol 940 ¹	0.75
	Triethanolamine	1.00
	Dye solution	0.05
	Perfume	0.10
	Laureth-23	0.10
25	DRO H ₂ O	q.s.

¹ cross-linked polyacrylic acid, commercially available from B. F. Goodrich

This batch is made by mixing the listed components together in a conventional manner.

30

EXAMPLE VIII

The following is a hair mousse composition representative of the present invention.

	<u>Component</u>	<u>Weight %</u>
	Polysiloxane-Grafted Polymer (Exp. A)	3.00
35	Ethanol	15.00

- 34 -

	Cocamine oxide	0.60
	D.C. 190 ¹	0.20
	Cocamide DEA	0.30
	Perfume	0.10
5	Isobutane	7.00
	DRO H ₂ O	q.s.

¹ dimethicone copolyol, commercially available from Dow Corning

The composition is made by blending all of the ingredients except isobutane at ambient temperature until well mixed. Aluminum aerosol cans are then filled with 95 parts of this batch, affixed with a valve which is crimped into position, and lastly pressure filled with 5 parts isobutane.

Examples IX-X

The following are hair styling/conditioning rinse compositions representative of the present invention.

	<u>Composition</u>	<u>IX</u>	<u>X</u>
	Citric Acid	0.02	0.02
	Sodium Citrate	0.09	0.09
	Cetyl Alcohol	0.12	0.12
20	Stearyl Alcohol	0.08	0.08
	Natrosol Plus CS Grade D-67 ¹	1.05	1.10
	Xanthan Gum ²	0.25	0.25
	Styling Polymer Premix		
	Polysiloxane-Grafted Polymer (Exp. B)	1.75	1.75
25	Octamethyl cyclotetrasiloxane	5.98	5.98
	Decamethyl cyclopentasiloxane	2.56	2.56
	Butyl Stearate	0.15	0.15
	Kathon CG	0.03	0.03
	Perfume	0.33	0.33
30	Conditioner Premix		
	DRO Water	12.18	11.88
	Adogen 442-100P ⁴	0.75	0.75
	Adogen 471 ⁵	--	0.60
	Stearyl Trimethyl		
35	Ammonium Chloride	0.30	--

- 35 -

Silicone Gum Premix			
	Decamethyl cyclopentasiloxane	1.42	1.42
	Polydimethyl Siloxane Gum ³	0.25	0.25
	Amodimethicone (Dow Corning Q2-8220)	--	0.10
5	DRO Water	q.s.	q.s.

¹Hydrophobically modified hydroxyethyl cellulose from Aqualon Corp.

²Readily dispersible xanthan gum

10 ³SE-76 gum available From General Electric

⁴Ditallow dimethyl ammonium chloride, Sherex Chemical Co., Dublin, Ohio, USA.

⁵Tallow trimethyl ammonium chloride, Sherex Chemical Co.

15 The styling polymer premix is prepared by combining the polymer, the octamethyl tetrasiloxane and decamethyl pentasiloxane, and butyl stearate.

The silicone gum premix is prepared by combining and mixing (in a separate vessel) the silicone gum and decamethyl cyclopentasiloxane until homogeneous.

20 The conditioner premix is prepared by combining and mixing (in a separate vessel) DRO water, any primary and secondary thickeners (premelted if necessary to ensure homogeneity) at 82° the silicone gum premix, and amodimethicone at 71°C, until homogeneous.

25 In another vessel, the DRO water is heated to 71°C. Citric acid, sodium citrate, cetyl alcohol, stearyl alcohol and Natrosol Plus CS grade D-67 are added and mixed until homogeneous. The xanthan gum is added and mixed until homogeneous. The styling polymer premix, Kathon CG and perfume are added and mixed until
30 homogeneous. The composition is further dispersed with an in-line homogenizer (such as Tekmar homogenizer) and then cooled to 38°C.

35 The conditioner premix is also further dispersed with an in-line homogenizer and cooled to 38°C and added to the final vessel, mixing until homogeneous to form the styling rinse composition.

- 36 -

When the compositions defined in Examples I-X are applied to hair in the conventional manner, they provide effective hair conditioning and styling/hold benefits without leaving the hair with a sticky/stiff feel.

5

EXAMPLE XI

An aerosol hair spray composition of the present invention is prepared as follows:

	<u>Component</u>	<u>Weight %</u>
	Polysiloxane-Grafted	4.00
10	Polymer (Exp. A)	
	Water	11.00
	Ethanol	63.50
	KOH (45% solution)	0.90
	Isobutane	15.00
15	Difluoroethane	6.00

All of the ingredients except for the propellants are mixed together at ambient temperature until the polymer is dissolved. The mixture is placed in an aerosol can which is then equipped with a conventional aerosol spray can valve, which is vacuum crimped in place. The propellants are then filled through the valve and the can is equipped with a conventional aerosol spray can activator.

25

30

35

- 37 -

WHAT IS CLAIMED IS:

1. A polymeric adhesive agent comprising a polysiloxane-grafted polymer, made by the polymerization of polysiloxane-containing monomers with non-polysiloxane-containing monomers, wherein said adhesive agent has a weight average molecular weight of at least 20,000 and contains from 1% to 50%, by weight, of polysiloxane-containing monomers, characterized in that said adhesive agent: has a weight percentage of silicon present as unreacted polysiloxane-containing monomer and polysiloxane grafted polymer having a viscosity at 25°C of below 10,000,000 centistokes based on the total silicon present as unreacted polysiloxane-containing monomer and polysiloxane-grafted polymer of 15% or less; and contains no more than 4%, by weight, of unreacted polysiloxane-containing monomer and polysiloxane-grafted polymer having a viscosity at 25°C of below 10,000,000 centistokes.

2. An adhesive agent as in Claim 1, wherein the weight percentage of unreacted polysiloxane-containing monomer and polysiloxane-grafted polymers having a viscosity at 25°C of below 10,000,000 centistokes based on the total silicon present as unreacted polysiloxane-containing monomer and polysiloxane-grafted polymer is 10% or less, preferably 5% or less, and said adhesive agent contains no more than 3%, preferably no more than 1%, by weight, of unreacted polysiloxane-containing monomer and polysiloxane-grafted polymer having a viscosity at 25°C of below 10,000,000 centistokes.

3. An adhesive agent as in Claim 1 or 2, wherein said weight average molecular weight of said adhesive agent is at least 75,000, preferably at least 100,000, more preferably from 100,000 to 750,000.

- 38 -

4. An adhesive agent as in Claim 1, 2, or 3, wherein said polymer comprises from 50% to 99%, by weight of the adhesive agent, of polymerizable, ethylenically unsaturated polymerizable monomers, and from 1% to 50% preferably from 2% to 25% of polysiloxane-containing monomers having a molecular weight of at least 1,000 and the general formula:



X is a vinyl group copolymerizable with the A and B monomers

Y is a divalent linking group

R is a hydrogen, hydroxyl, lower alkyl, aryl, alkaryl, alkylamino, or alkoxy

Z is a monovalent siloxane polymeric moiety having a number average molecular weight of at least 500, is essentially unreactive under copolymerization conditions, and is pendant from said vinyl polymeric backbone after polymerization

n is 0 or 1, and

m is an integer from 1 to 3.

5. An adhesive agent as in Claim 4, wherein said non-polysiloxane-containing monomer is a free radically polymerizable vinyl .

6. An adhesive agent as in Claim 4 or 5, wherein said non-polysiloxane-containing monomers are selected from the group consisting of hydrophobic monomers selected from the group consisting of acrylic acid esters of C₁-C₁₈ alcohols, methacrylic acid esters of C₁-C₁₈ alcohols, styrene, polystyrene macromer, vinyl acetate, vinyl chloride, vinyl propionate, vinylidene chloride, alpha-methylstyrene, t-butylstyrene, butadiene, cyclohexadiene, ethylene propylene, vinyl toluene, acrylic acid, methacrylic acid, N,N-dimethylacrylamide, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, methacrylamide,

- 39 -

N-t-butyl acrylamide, maleic acid, maleic anhydride, half esters of maleic anhydride, crotonic acid, itaconic acid acrylamide, acrylate alcohols, hydroxyethyl methacrylate, diallyldimethyl ammonium chloride, vinyl pyrrolidone, vinyl ethers, maleimides, vinyl pyridine, vinyl imidazole, styrene sulfonate, allyl alcohol, vinyl alcohol, vinyl caprolactam, and mixtures thereof, and hydrophilic monomers selected from the group consisting of acrylic acid, methacrylic acid, N,N-dimethylacrylamide, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, methacrylamide, N-t-butyl acrylamide, maleic acid, maleic anhydride and its half esters, crotonic acid, itaconic acid, acrylamide, acrylate alcohols, hydroxyethyl methacrylate, diallyldimethyl ammonium chloride, vinyl pyrrolidone, vinyl ethers, maleimides, vinyl pyridine, vinyl imidazole, other polar vinyl heterocyclics, styrene sulfonate, allyl alcohol, vinyl alcohol, vinyl caprolactam, salts of the above acids and amines, and mixtures thereof.

7. An adhesive agent as in Claim 6, wherein said hydrophobic monomers are selected from the group consisting of t-butyl acrylate, t-butyl methacrylate, and mixtures thereof.

8. An adhesive agent as in Claim 6 or 7, wherein said hydrophilic monomers are selected from the group consisting of acrylic acid, N,N-dimethylacrylamide, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, vinyl pyrrolidone, salts of the above acids and amines, and mixtures thereof.

9. An adhesive agent as in Claim 6, 7, or 8, comprising from 0% to 85%, by weight, of said hydrophobic monomers, from 14% to 95% of said hydrophilic monomers, and from 1% to 40% of said polysiloxane-containing monomers, preferably from 5% to 70% of said hydrophobic monomers, from 29% to 80% of said

- 40 -

hydrophilic monomers, and from 2% to 25% of said polysiloxane-containing monomers.

10. An adhesive agent as in Claim 6, 7, or 8, comprising from 0% to 70%, by weight, of said hydrophilic monomers, from 20% to 80% of said hydrophobic monomers, and from 1% to 40% of said polysiloxane-containing monomers, preferably from 5% to 70% of said hydrophobic monomers, from 20% to 60% of said hydrophilic monomers, and from 2% to 25% of said polysiloxane-containing monomers.

11. A hair care composition useful for styling hair, comprising the adhesive agent of Claim 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10 and a carrier suitable for application to the hair.

12. A hair care composition as in Claim 11, in the form of liquid suitable for spray application to the hair, wherein said carrier comprises water, C₁-C₈ monohydric alcohol, or a mixture thereof.

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵: A61K 7/08, 7/48, 7/13	A1	(11) International Publication Number: WO 95/00106 (43) International Publication Date: 5 January 1995 (05.01.95)
(21) International Application Number: PCT/US94/05245 (22) International Filing Date: 11 May 1994 (11.05.94) (30) Priority Data: 9312618.3 18 June 1993 (18.06.93) GB (71) Applicant (for all designated States except US): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): WELCH, Rosemary, Jane [GB/GB]; 15 Thorncroft Englefield Green, Surrey TW20 0SB (GB). DODSWORTH, Emma, Louise [GB/GB]; Stylehurst Cottage, Weare Street, Capel, Surrey RH5 5JD (GB). CHAMBERS, Gillian [GB/GB]; Flat 5, 6 Avenue Road, Staines, Middlesex TW18 3AW (GB). (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45202 (US).		(81) Designated States: AU, BR, CA, CN, JP, KR, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: HAIR COSMETIC COMPOSITIONS (57) Abstract A liquid hair cosmetic composition comprising: (a) from about 0.1 % by weight to about 10 % by weight (acid basis) of a silicone-containing polycarboxylic acid copolymer having a vinyl polymeric backbone, and having grafted to the backbone a silicone-containing macromer having a weight average molecular weight of from about 1,000 to about 50,000; (b) a mixed neutralising system comprising an organic and an inorganic base, wherein the organic base is at a level sufficient to neutralise from about 0.01 % to about 15 % of the acid groups on the silicone-containing copolymer while the inorganic base is at a level sufficient to neutralise from about 25 % to about 80 % of the acid groups on the silicone-containing copolymer; and (c) from 0 % to about 10 % by weight of water; and (d) the balance comprising a carrier suitable for application to hair. The liquid hair cosmetic products have an improved clarity and demonstrate excellent hair styling benefits in addition to hair feel attributes and ease of brush out.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

HAIR COSMETIC COMPOSITIONS

Technical Field

The present invention relates to hair cosmetic compositions. More particularly, this invention relates to liquid hair cosmetic compositions containing silicone grafted hair styling polymer neutralised with a mixture of inorganic and organic neutralising agents and having improved product stability and style retention properties.

Background Of The Invention

The desire to have the hair retain a particular shape is widely held. A common methodology for accomplishing this is applying hair styling, or "setting" compositions to the hair, typically to damp or dry hair. These compositions provide temporary setting benefits, and should be removable by water and/or by shampooing. The materials used in the compositions to provide the setting benefits are generally applied in the form of mousses, gels, lotions or sprays.

High levels of style retention, or hold, are typically expected from hair styling compositions applied as a spray. Style retention is typically achieved by the use of resins, such as AMPHOMER, supplied by

National Starch, and GANTREZ SP 225, supplied by GAF. As used in commercially sold hairspray products, these resins generally have a weight average molecular weight of from about 40,000 to about 150,000. When such resins are incorporated into pump and aerosol hairsprays, they can provide suitable style retention attributes. However, such resins are found to be deficient in the area of hair feel and can give a stiff hair feel.

Recently, it has been found that certain neutralisable polymers having silicone macromer portions can provide good style retention benefits to the hair while also providing improved hair feel. In other words, such silicone macromer-containing polymers can impart a tactile sense of softness and conditioning to the hair relative to conventional, non-silicone-containing resins without the tacky hair feel traditionally associated with non-silicone hair fixative polymers. Silicone macromer-containing hair styling polymers and formulations containing them are disclosed, for example, in EP-A-0,408,311 A2 issued January 11th 1991, Hayama, et al., US-A-5,061,481, issued October 29th 1991, Suzuki et al., US-A-5,106,609, Bolich et al., issued April 21st 1992, US-A-5,100,658, Bolich et al., issued March 31st 1992, US-A-5,100,657, Ansher-Jackson, et al., issued March 31st 1992 and US-A-5,104,646, Bolich et al., issued April 14th 1992.

It is well known that at least partial neutralisation of the silicone macromer containing hair styling polymer is necessary to maximise its utility in hair styling compositions. Typically, silicone grafted copolymers neutralised with an inorganic neutraliser exhibit good solubility in hairspray compositions containing 15% water. However, it has now been found that such inorganic neutralised systems are less soluble in compositions which contain lower levels of water and lead to hazy, colloidal systems. It has also been found that by using selected mixtures of inorganic and organic neutralisers in liquid hair cosmetic compositions, systems of excellent clarity can be achieved.

Thus a need exists for hair styling compositions which have a clear appearance, deliver effective style retention, impart a hair conditioning effect, have a non-sticky hair feel, are easily brushed out and at the same

time have stable product and viscosity characteristics and remain fully stable under long term and stressed temperature storage.

Summary of the Invention

According to one aspect of the invention, there is provided a liquid hair cosmetic composition comprising:-

- (a) from about 0.1 % by weight to about 10% by weight (acid basis) of a silicone-containing polycarboxylic acid copolymer having a vinyl polymeric backbone, and having grafted to the backbone a silicone containing macromer having a weight average molecular weight of from about 1,000 to about 50,000;
- (b) a mixed neutralising system comprising an organic and an inorganic base, wherein the organic base is at a level sufficient to neutralise from about 0.01 % to about 15% of the acid groups on the silicone-containing copolymer while the inorganic base is at a level sufficient to neutralise from about 25% to about 80% of the acid groups on the silicone-containing copolymer;
- (c) from 0% to about 10% by weight of water; and
- (d) the balance comprising a carrier suitable for application to hair.

The preferred neutralising systems for use herein comprise a combination of organic and inorganic base. From about 30% to about 95% more preferably from about 55% to about 75%, most preferably from about 60% to about 70% of the acidic groups of the polymer should be neutralised with the chosen mixed neutralising system, the level of neutralisation being determined in the manner described herein below.

The essential, as well as the optional, components of the present invention are described below. All levels and ratios are on a weight basis unless otherwise specified.

Silicone-Containing Copolymer

The compositions of the present invention contain from about 0.1 % to about 10.0%, preferably from about 0.5% to about 8.0% and especially from about 1 % to about 6% of specifically-defined silicone-containing copolymers. It is these polymers which provide the unique hair conditioning and hair setting characteristics of the present invention. The polymers preferably have a weight average molecular weight of from about 10,000 to about 1,000,000, preferably from about 30,000 to about 300,000, most preferably from about 90,000 to about 300,000 and, preferably, have a Tg of at least about -20°C. As used herein, the abbreviation "Tg" refers to the glass transition temperature of the non-silicone backbone, and the abbreviation "Tm" refers to the crystalline melting point of the non-silicone backbone, if such a transition exists for a given polymer.

The molecular weights and molecular weight distributions of the polymers utilised in the compositions according to the present invention are determined by Size Exclusion Chromatography (SEC). In practise, polymers comprise a distribution of molecular weight species that gives rise to their unique properties. Separation of the molecules is accomplished by Size Exclusion Chromatography (SEC) using a crosslinked polystyrene -divinylbenzene column (MW range = $100 - 10^7$) with a differential refractive index detector and a differential viscometer. A universal calibration curve is prepared from monodispersed polystyrene standards of known molecular weight (MW) and molecular weight distribution (MWD). MW and MWD of the given polymer are determined based on concentration and viscosity responses relative to the calibration.

Preferred polymers comprise a vinyl polymeric backbone, preferably having a Tg above about -20°C and, grafted to the backbone, a silicone containing macromer having a weight average molecular weight of from about 1,000 to about 50,000, preferably from about 5,000 to about 40,000, most preferably from about 10,000 to about 20,000. The polymer is such that when it is formulated into the finished hair care composition, when dried, the polymer phase separates into a

discontinuous phase which includes the silicone containing macromer and a continuous phase which includes the backbone. It is believed that this phase separation property provides a specific orientation of the polymer on hair which results in the desired hair conditioning and setting benefits.

In its broadest aspect, the copolymers utilized in the present application comprise a silicone-containing monomer (hereafter identified as C) together with a hydrophilic carboxylate-containing monomer (B) and optionally a lipophilic monomer (A).

Examples of useful copolymers and their preparation are described in detail in US-A-4,693,935, Mazurek, issued September 15th 1987, and US-A-4,728,571, Clemens et al., issued March 1st 1988. These copolymers comprise monomers A, B and C as defined above. In preferred embodiments, A comprises at least one free radically polymerizable vinyl monomer or monomers and B comprises at least one reinforcing monomer copolymerizable with A and selected from the group consisting of carboxylate-containing monomers and macromers having a T_g or a T_m above about -20°C . B can be up to about 98%, preferably up to about 80%, more preferably up to about 30%, of the total monomers in the copolymer. Monomer C comprises from about 0.1% to about 50.0% of the total monomers in the copolymer.

Representative examples of A (hydrophobic) monomers are the acrylic or methacrylic acid esters of C_1 - C_{18} alcohols, such as methanol, ethanol, methoxy ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 1-methyl-1-butanol, 3-methyl-1-butanol, 1-methyl-1-pentanol, 2-methyl-1-pentanol, 3-methyl-1-pentanol, t-butanol (2-methyl-1-propanol), cyclohexanol, neodecanol, 2-ethyl-1-butanol, 3-heptanol, benzyl alcohol, 2-octanol, 6-methyl-1-heptanol, 2-ethyl-1-hexanol, 3,5-dimethyl-1-hexanol, 3,5,5-trimethyl-1-hexanol, 1-decanol, 1-dodecanol, 1-hexadecanol, 1-octadecanol, and the like, the alcohols having from about 1-18 carbon atoms with the average number of carbon atoms being from about 4-12; styrene; polystyrene macromer; vinyl acetate; vinyl chloride; vinylidene chloride; vinyl propionate; alpha-methylstyrene; t-butylstyrene; butadiene;

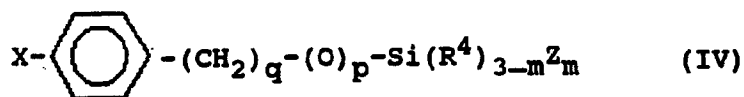
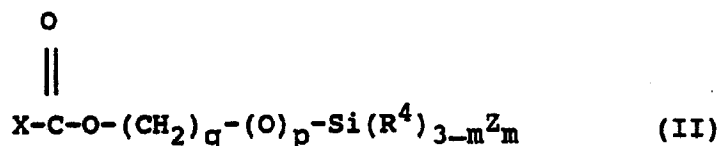
cyclohexadiene; ethylene; propylene; vinyl toluene; and mixtures thereof. Preferred A monomers include n-butyl methacrylate, isobutyl methacrylate, 2-ethylhexyl methacrylate, methyl methacrylate, t-butylacrylate, t-butylmethacrylate, and mixtures thereof.

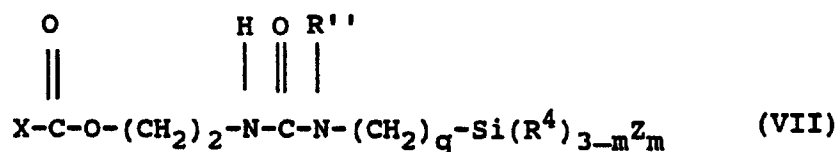
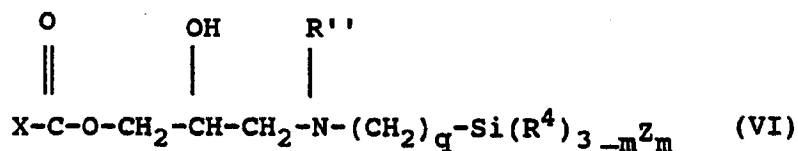
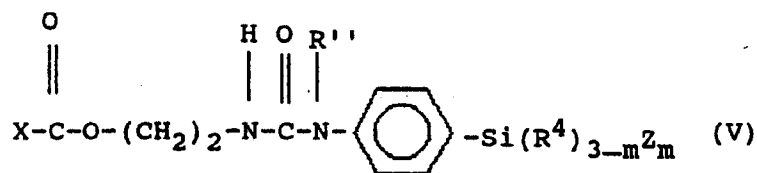
Representative examples of B (hydrophilic) neutralisable monomers containing a carboxyl moiety include acrylic acid, methacrylic acid, maleic acid, maleic anhydride, half esters of maleic anhydride, crotonic acid, and itaconic acid. Preferred B monomers include acrylic acid and methacrylic acid and mixtures thereof.

The C monomer preferably has the general formula (I):



wherein X is a vinyl group copolymerizable with the A and B monomers; Y is a divalent linking group; R is hydrogen, C₁-C₄ alkyl, aryl, alkyl amino, tri(C₁-C₄ alkyl)siloxy or C₁-C₄ alkoxy; Z is a monovalent siloxane polymeric moiety; n is 0 or 1; and m is an integer from 1 to 3. C has a number average molecular weight of, at least 500, preferably from 1,000 to 50,000. Preferably, the C monomer is selected from one or more monomers having the general formulae (II to VII):





In these structures, m is 1, 2 or 3 (preferably m = 1); p is 0 or 1; R'' is alkyl or hydrogen; q is an integer from 2 to 6; X is



R¹ is hydrogen or -COOH (preferably R¹ is hydrogen); R² is hydrogen, methyl or -CH₂COOH (preferably R² is methyl); Z is



R⁴ is alkyl, alkoxy, alkylamino, aryl, or hydroxyl (preferably R⁴ is alkyl); and r is an integer from 5 to 700, preferably from 50 to 500, more preferably from 150 to 300. Of the above, formula II is preferred, particularly when p = 0 and q = 3.

The polymers utilized herein generally comprise from 0% to about 98% (preferably from about 5% to about 92%, more preferably from about

50% to about 90%) of monomer A, from about 1% to about 98% (preferably from about 7.5% to about 80%) of monomer B, and from about 0.1% to about 50% (preferably from about 0.5% to about 40%, most preferably from about 2% to about 25%) of monomer C. The combination of the A and B monomers preferably comprises from about 50.0% to about 99.9% (more preferably about 60% to about 99.5%, most preferably from about 75% to about 98%) of the polymer.

Preferred silicone-containing copolymers for use herein are selected from:

acrylic acid/n-butylmethacrylate/polydimethylsiloxane (PDMS)
macromer-20,000 molecular weight (mw) (10/70/20 w/w/w)

acrylic acid/isobutyl methacrylate/PDMS macromer - 20,000 mw
(20/60/20 w/w/w)

acrylic acid/PDMS macromer - 20,000 mw (80/20 w/w)

t-butylacrylate(tBA)/acrylic acid(AA)/PDMS macromer - 10,000 mw
(60/20/20)

acrylic acid/isobutyl methacrylate/PDMS macromer - 20,000 mw
(10/70/20);

acrylic acid/methyl methacrylate/PDMS macromer - 20,000 mw
(40/40/20);

acrylic acid/isopropyl methacrylate/PDMS macromer - 20,000 mw
(25/65/15);

acrylic acid/methoxyethyl methacrylate/PDMS macromer 20,000 mw
(60/25/15);

acrylic acid/PDMS macromer - 20,000 mw (80/20);
and mixtures thereof.

The silicone-containing copolymers described above can be synthesized by free radical polymerization of silicone- or polysiloxane-containing monomers with non-silicone- or non-polysiloxane-containing monomers. The general principles of free radical polymerization methods are well understood. See, for example, Odian, "Principles of Polymerization", 2nd edition, John Wiley & Sons, 1981, pp. 179 - 318.

In compositions according to the invention it can be desirable to purify the silicone containing copolymer by removing unreacted silicone-containing monomer and silicone macromer-grafted polymer with viscosities at 25°C of about 10,000,000 centistokes and less. This can be done, for example, by hexane extraction. After drying the resin from its reaction solvent, hexane extraction of the reaction product can be performed by adding an excess of hexane to the reaction product and heating to near the T_g of the non-silicone portion of the polymer. The mixture is held at this temperature with stirring for about 30 minutes and cooled to room temperature. The hexane is removed by vacuum suction. Two more hexane extraction cycles are preferably conducted in the same manner as above. After the third cycle, residual hexane remaining with the product is removed by distillation and vacuum drying.

Low molecular weight polysiloxane-containing monomer and polymer is solubilized by supercritical carbon dioxide and transported away from the remaining polymer via a transfer line, which is maintained at identical temperature and pressure as the extraction vessel. The extracted materials are collected in an extraction vessel. Following extraction, the system is depressurised and dry, extracted polymer is recovered from the extraction vessel.

Neutralising System

The hair styling polymers, herein are preferably utilised in at least partially neutralised form in order to aid shampoo removability of the liquid hair cosmetic compositions. The present development relates to the neutralisation of a hair fixative polymer (eg silicone grafted tBA/AA copolymer) with a combination of neutraliser systems, specifically an inorganic base, preferably KOH, and an organic base, preferably AMP

(amino methyl propanol) in hairspray and other hair cosmetic products. In particular the present development relates to improving the clarity of hairspray and other hair cosmetic products containing low levels of water, approximately 0 - 10%, preferably 0 - 7% water. It has been discovered that addition of a very small % of organic base dramatically improves the solubility and clarity of low water containing hairspray products containing silicone-grafted copolymer. In addition use of organic base in these levels does not increase the sticky hair feel. This is surprising as neutralisation with AMP traditionally leads to sticky hair feel negatives. Additional benefits include improved hold via increased polymer bond flexibility whilst maintaining ease of wash-out and reduced negatives such as rough hair feel associated with inorganic (non-plasticising) neutralisers eg. KOH. Furthermore compositions according to the invention provide excellent hair conditioning benefits. In total from about 30% to about 95%, preferably from about 55% to about 75%, most preferably from about 60% to about 70% of the acidic monomers of the polymer should be neutralised.

Optimum neutralising systems for compositions according to the invention contain a mixture of inorganic and organic bases at a level sufficient to provide from about 25% to about 80%, preferably about 40% to about 70%, more preferably about 55% to about 65% neutralisation of the acid groups on the silicone containing copolymer with inorganic neutraliser and from about 0.01% to about 15%, preferably about 0.5% to about 8%, more preferably about 1% to about 6% neutralisation of the acid groups on the silicone containing copolymer with organic neutraliser. In preferred embodiments the weight ratio of inorganic base to organic base is in the range of from 1000 : 1 to 4 : 1, preferably from 100 : 1 to 5 : 1, more preferably from 50 : 1 to 6 : 1.

The particular effects of such systems are improved product clarity; improved solubility in ethanol; improved long term stability of the product and improved style retention via increased polymer bond flexibility.

Any conventionally used base, organic or inorganic, may be used for neutralisation of acidic polymers providing they are utilised in mixtures as specified herein. Hydroxides of alkali, alkaline earth and amino alcohols

are suitable neutralisers for use in the present liquid hair cosmetic compositions.

Examples of suitable organic neutralising agents which may be included in the hair cosmetic compositions of the present invention include amines, especially amino alcohols such as 2-amino-2-methyl-1,3-propanediol (AMPD), 2-amino-2-ethyl-1,3-propanediol (AEPD), 2-amino-2-methyl-1-propanol (AMP), 2-amino-1-butanol (AB), monethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), monoisopropanolamine (MIPA), diisopropanolamine (DIPA), triisopropanolamine (TIPA), dimethyl steramine (DMS) and amino methyl propanol (AMP) and mixtures thereof.

Preferred neutralising agents for use in hairspray compositions of the present invention are potassium and sodium hydroxides and aminomethyl propanol (AMP).

The amount in grams of inorganic and organic base (Z) required to neutralise a polymer can be deduced from calculations which take into account the acid value of the polymer (A); amount of polymer (W); mol wt of the base (B); mol wt of the acidic moiety (M) and the degree of neutralisation required (N).

$$Z(g) = W \times A/100 \times 1/M \times B \times N\%$$

In the following example the amount of KOH required to neutralise 2.6g of acrylic acid co-polymer (with acid value of 20) to a level of 60% neutralisation is calculated.

$$Z(g) = 2.6 \times 20/100 \times 1/72 \times 56 \times 0.60$$

$$Z = 0.242 \text{ g}$$

Note the acid value can be experimentally determined by titrating a specific amount of the polymer with base or theoretically by considering

the original acidic content of the co-polymer i.e. a polymer with 20% of acid monomer has an acid value of 20.

As described earlier herein, use of the herein defined mixed inorganic/organic neutralising system for at least partial neutralisation of the silicone grafted copolymer leads to liquid hair cosmetic compositions of dramatically improved clarity. Product clarity is measured using a Digital Direct Reading Turbidimeter. Using this equipment the turbidity of test samples is measured by calibration against two known references (Orbeco-Hellige Transfer Turbidity Standards) which give turbidity readings of 0 and 999 respectively. Typical turbidity measurement for opaque systems neutralised with inorganic neutraliser can be as high as 700.

In contrast the clarity of the mixed organic/inorganic neutralised systems according to the invention registers a turbidity measurement in the range from 0 to 50, preferable 0 to 40, more preferably 0 to 30.

The liquid hair cosmetic compositions of the present invention also include a carrier. This can comprise any of those conventionally used in resin hairspray formulations inclusive of solvents, propellants and other optional ingredients of liquid hair cosmetics. The carrier is generally present in the liquid hair cosmetic compositions at from about 70% to about 99.8%, preferably from about 78% to about 99% by weight. More preferably, the carrier is present at from about 80% to about 98% by weight of the total composition.

Organic solvents suitable for use in the carrier of the present compositions include C₁-C₆ alkanols, carbitol, acetone and mixtures thereof. C₁-C₆ alkanols preferred for use in the present compositions are C₂-C₄ monohydric alcohols such as ethanol, isopropanol and mixtures thereof.

Liquid hair cosmetic compositions according to the present invention contain from 0% to about 10% by weight of water, preferably from 0% to about 7% by weight of water. It is a feature of the invention that utilising mixed neutraliser systems as defined herein, liquid hair cosmetic

compositions having excellent clarity are achieved at zero or low levels of water content.

Plasticizer

The performance of the liquid hair cosmetic compositions according to the invention can be improved through the optional incorporation of a nonvolatile plasticizer into the composition. The plasticizer will generally be present in the compositions at up to a level of 25%, preferable from 1% to 20%, more preferably from 1% to 15%. As used herein, "nonvolatile" in regard to plasticizers means that the plasticizer exhibits essentially no vapour pressure at atmospheric pressure and 25°C. The polymer-liquid vehicle solution should not suffer from substantial plasticizer weight loss while the hair cosmetic carrier is evaporating, since this may excessively reduce plasticization of the polymer during use. The plasticizers for use herein should generally have boiling points of about 250°C or higher.

Plasticizers are well known in the art and are generally described in Kirk-Othmer Encyclopedia of Chemical Technology, second edition, Volume 15, pp. 720-789 (John Wiley & Sons, Inc. New York, 1968) under the topic heading "Plasticizers", and by J. Kern Sears and J. R. Darby in the text The Technology of Plasticizers (John Wiley & Sons, Inc., New York, 1982). See especially in the Appendix of Sears/Darby Table A.9 at pages 983-1063 where a wide variety of plasticizers are disclosed.

Plasticizers suitable for use in compositions of the present invention include both cyclic and acyclic nonvolatile materials. Suitable categories of nonvolatile plasticizers include adipates, phthalates, isophthalates, azelates, stearates, citrates, trimellitates, silicone copolyols, iso C₁₄ - C₂₂ alcohols, methyl alkyl silicones, carbonates, sebacates, isobutyrate, oleates, phosphates, myristates, ricinoleates, pelargonates, valerates, camphor, glycols, amine derivatives, selected short chain alcohols and castor oil.

Particularly preferred plasticizers for use herein include glycol and citrate based plasticizers such as propylene glycol, dipropylene glycol ,

acetyl tri-n-butyl citrate, tri-n-butyl and acetyl tri-2-ethoxyhexyl citrate (as supplied by Pfizer under the trade name Citroflex RTM) and also glycerin, amino methyl propanol (AMP), diisobutyladipate (DIBA) and isopropanol.

Propellant

The present compositions can be formulated as hairsprays in aerosol or non-aerosol forms. If an aerosol hairspray is desired, a propellant must be included in the composition. This agent is responsible for expelling the other materials from the container and forming the hairspray character.

The propellant gas can be any liquefiable gas conventionally used for aerosol containers. Preferably the density of the propellant or mixture thereof is less than 1 so that pure propellant is not emitted from the container. Examples of materials that are suitable for use as propellants are trichlorofluoromethane, dichlorodifluoromethane, dichlorotetrafluoroethane, monochlorodifluoromethane, trichlorotrifluoroethane, dimethylether e.g. Dimel 152A (RTM) supplied by Du Pont, propane, n-butane, isobutane, used singly or admixed and propane butane e.g. CAP 80 (RTM). Dimel 152A (RTM) and propane butane are preferred.

The amount of the propellant gas is governed by normal factors well known in the aerosol art. For hairsprays the level of propellant is generally from about 10% to about 40%, preferably from about 20% to about 30%, of the total composition. If a propellant such as dimethylether utilizes vapor pressure suppressant (e.g., trichloroethane or dichloromethane) the amount of suppressant is included as part of the propellant.

The hair spray compositions of the present invention can be made using conventional formulation and mixing techniques. Compositions of the present invention can be made by adding the polymer to ethanol and mixing for several hours until dissolved. Plasticizer and neutralising ingredients are then added and the resulting solution is stirred. Any

remaining ingredients such as water, ethanol and perfume can then be added.

Methods of making the hair cosmetic compositions of the present invention are described more specifically in the examples.

Alternatively, pressurised aerosol dispensers can be used where the propellant is separated from contact with the hairspray composition by use of specialised containers such as a two compartment can of the type sold under the tradename SEPRO from Americal National Can Corp.

Other suitable aerosol dispensers are those characterized by the propellant being compressed air which can be filled into the dispenser by means of a pump or equivalent device prior to use. Such dispensers are described in US-A-4,077,441, March 7th 1978, Olofsson and US-A-4,850,577, July 25th 1989, TerStege. Compressed air aerosol containers suitable for use are also currently marketed by The Procter & Gamble Company under their tradename VIDAL SASSOON AIRSPRAY (RTM) hairsprays.

Conventional non-aerosol pump spray dispensers, i.e., atomizers, can also be used.

Other Ingredients

The liquid hair cosmetic compositions of the present invention can also contain a variety of non-essential, optional components such as preservatives, surfactants, block polymers, thickeners and viscosity modifiers, electrolytes, fatty alcohols, pH adjusting agents, perfume oils, perfume solubilizing agents, sequestering agents; emollients; lubricants and penetrants such as various lanolin components; protein hydrolysates and other protein derivatives; ethylene adducts and polyoxyethylene cholesterol; sunscreens and volatile and non-volatile silicone fluids. Such conventional optional ingredients are well known to a person skilled in the art, e.g. surfactants such as anionics (e.g., sodium alkyl sulphates, nonionics (amine oxides); amphoterics (aliphatic secondary or tertiary amine derivatives) zwitterionics (aliphatic quaternary ammonium; phosphonium or sulphonium derivatives) and fluorinated surfactants (e.g.

Zonyl FSK) (RTM); thickeners and viscosity modifiers such as diethanolamides of long chain fatty acids; block polymers of ethylene oxide and propylene oxide such as Pluronic (RTM) F88 offered by BASF Wyandotte; fatty alcohols such as cetearyl alcohol; viscosity modifiers such as sodium chloride, sodium sulphate, and ethyl alcohol; electrolyte such as earth and alkaline-earth metal salts; quaternary ammonium ions and cationic amines and halogen ions; pH adjusting agents such as citric acid, succinic acid, sodium hydroxide and triethanolamine; perfume oils such as Florasynth (RTM) perfumes; perfume oil solubilizers such as polyethylene glycol fatty acid esters and sequestering agents such as ethylenediamine tetraacetic acid. Each of these optional materials can be present at a level of from about 0.05% to about 5%, preferably from about 0.1% to about 3% by weight of composition.

The liquid hair cosmetic compositions of the present invention are used in conventional ways to provide the hair styling/holding benefits of the present invention. Such method generally involves spraying an effective amount of the product to dry or damp hair before or after the hair is styled, or both. By "effective amount" is meant an amount sufficient to provide the hair volume and style benefits desired considering the length and texture of the hair.

The invention is illustrated by the following non-limiting examples.

In the examples, all concentrations are on a 100% active basis, unless otherwise stated and the abbreviations have the following designation:

Hair Styling Polymer - 60% t-butyl acrylate/20% acrylic acid/20% silicone PDMS. Weight average molecular weight (measured by SEC) of 150,000.

KOH - Potassium hydroxide solution, containing 45% potassium hydroxide and 55% water and minors.

AMP - 2-Amino-2-methyl-1-propanol.

DRO Water - Double reverse osmosis water

Solvent - Ethanol

Examples I-VI

The following are liquid hair cosmetic compositions in the form of hairspray compositions suitable for pump spray dispensers and which are representative of the present invention:

	I	II	III	IV	V	VI
Hair Styling Polymer	3.0	2.0	4.0	6.0	2.0	5.0
% poly KOH neutralised	60	55	60	65	60	55
% poly AMP neutralised	5	5	8	2	10	5
DRO Water	0	3.0	7.0	7.0	10.0	0
Balance	-----to 100 percent with ethanol-----					

The balance contains ethanol and optional ingredients such as plasticizer, perfume and surfactants.

The hairspray formulations are prepared by adding the polymer directly to the ethanol. A magnetic or air driven stirrer is used to mix the ingredients until the polymer is dissolved, typically about 1 to 2 hours. The neutralizing agent (KOH and AMP) is then added and mixed into the premix. Then, the optional ingredients and water, as may be applicable, are mixed into the composition.

The above compositions provide effective style retention, deliver a hair conditioning effect and have excellent clarity.

Examples VII-XII

The following are liquid hair cosmetic compositions in the form of hairspray concentrate compositions suitable for aerosol dispensers and which are representative of the present invention:

	VII	VIII	IX	X	XI	XII
Hair Styling Polymer	4.0	2.0	5.0	6.0	3.0	7.0
% poly KOH neutralised	55	60	60	65	55	65
% poly AMP neutralised	5	8	2	2	5	5
DRO Water	0	7.0	10.0	7.0	0	0
Balance	----- to 100 percent with solvent -----					

As in examples I to VI the balance can contain ethanol and optional ingredients such as plasticizer, perfume and surfactants. The above compositions are prepared as in Examples I-VI. The concentrates are packaged in conventional aerosol spray cans and are charged with a conventional liquifiable propellant such as CAP 80 (RTM) at a propellant:concentrate weight ratio of 23:77.

The above compositions will have excellent clarity and stability characteristics and when applied to the hair, provide good hair styling and conditioning benefits.

WHAT IS CLAIMED IS:

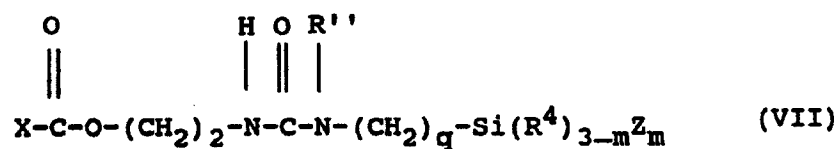
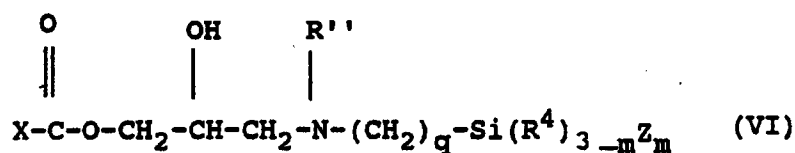
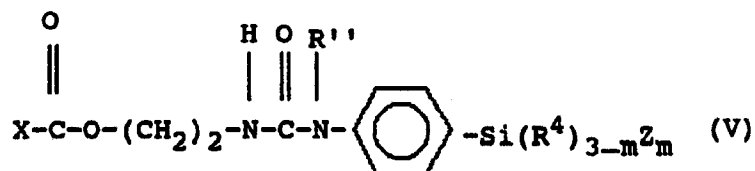
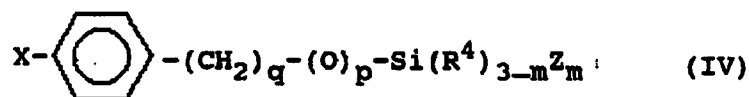
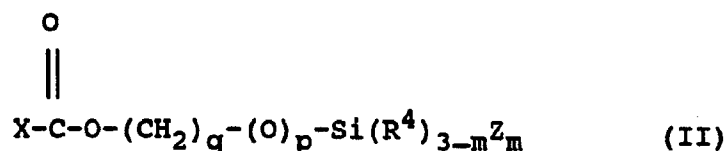
1. A liquid hair cosmetic composition comprising:-
 - (a) from about 0.1% by weight to about 10% by weight (acid basis) of a silicone-containing polycarboxylic acid copolymer having a vinyl polymeric backbone, and having grafted to the backbone a silicone-containing macromer having a weight average molecular weight of from about 1,000 to about 50,000;
 - (b) a mixed neutralising system comprising an organic and an inorganic base, wherein the organic base is at a level sufficient to neutralise from about 0.01% to about 15% of the acid groups on the silicone-containing copolymer while the inorganic base is at a level sufficient to neutralise from about 25% to about 80% of the acid groups on the silicone-containing copolymer; and
 - (c) from 0% to about 10% by weight of water; and
 - (d) the balance comprising a carrier suitable for application to hair.
2. A liquid hair cosmetic composition according to Claim 1 wherein the silicone-containing macromer has the general formula (I):



wherein X is a vinyl group; Y is a divalent linking group; R is hydrogen, alkyl, aryl, alkylamino, trialkylsiloxy or alkoxy; Z is a monovalent siloxane polymeric moiety having a number average molecular weight of at least about 500; n is 0 or 1; and m is an integer from 1 to 3.

3. A liquid hair cosmetic composition according to Claim 1 or 2 wherein the silicone-containing copolymer has a weight average

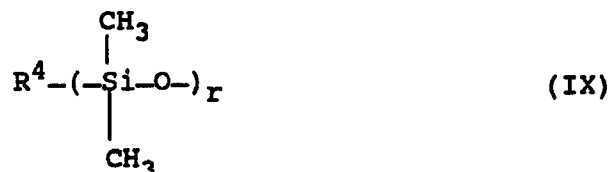
molecular weight of from 10,000 to 1,000,000 comprising a hydrophilic carboxylate containing monomer (B), optionally a lipophilic, low polarity, free-radically polymerizable vinyl monomer (A) which is copolymerizable with B, and a silicone-containing macromer (C) having a weight average molecular weight of from 1,000 to 50,000, preferably from 5,000 to 40,000, based on polydimethylsiloxane and wherein the macromer (C) is selected from one or more monomers having the general formulae (II - VII):



wherein m is 1, 2 or 3; p is 0 or 1; R" is alkyl or hydrogen; q is an integer from 2 to 6; X is



R¹ is hydrogen or -COOH; R² is hydrogen, methyl or -CH₂COOH; Z is



R⁴ is alkyl, alkoxy, alkylamino, aryl or hydroxyl; and r is an integer from 5 to 700; and wherein the silicone-containing copolymer comprises from 0% to 98% monomer A, from 1% to 98% monomer B, and from 0.1% to 50% monomer C.

4. A liquid hair cosmetic composition according to any of Claims 1 to 3 wherein the silicone-containing copolymer comprises from 5% to 92% by weight monomer A, from 7.5% to 80% by weight monomer B, and from 0.1% to 50% monomer C.
5. A liquid hair cosmetic composition according to any of Claims 1 to 4 wherein monomer A is selected from acrylic acid esters of C₁-C₁₈ alcohols, methacrylic acid esters of C₁-C₁₈ alcohols, styrene, polystyrene macromer, vinyl acetate, vinyl chloride, vinyl propionate, vinylidene chloride, alpha-methylstyrene, t-butylstyrene, butadiene, cyclohexadiene, ethylene propylene, vinyl toluene, and mixtures thereof; and is preferably selected from n-butylmethacrylate, isobutylmethacrylate, 2-ethylhexylmethacrylate, methylmethacrylate, t-butylacrylate, t-butylmethacrylate, and mixtures thereof.
6. A liquid hair cosmetic composition according to any of Claims 1 to 5 wherein monomer B is selected from acrylic acid, methacrylic

acid, maleic acid, maleic anhydride, half esters of maleic anhydride, crotonic acid, itaconic acid and mixtures thereof; and is preferably selected from acrylic acid and methacrylic acid and mixtures thereof.

7. A liquid hair cosmetic composition according to any of Claims 3 to 6 wherein the silicone containing macromer has the general formula (II) in which $p = 0$ and $q = 3$, m is 1, R^4 is alkyl, R^1 is hydrogen and R^2 is methyl.

8. A liquid hair cosmetic composition according to any of Claims 1 to 7 wherein the silicone-containing copolymer is selected from:

acrylic acid/n-butylmethacrylate/polydimethylsiloxane (PDMS) macromer - 20,000 molecular weight (mw) (10/70/20);
acrylic acid/isobutyl methacrylate/PDMS macromer - 20,000 mw (20/60/20 w/w/w)
acrylic acid/PDMS macromer - 20,000 mw (80/20 w/w)
t-butylacrylate(tBA)/acrylic acid(AA)/PDMS macromer - 10,000 mw (60/20/20)
acrylic acid/isobutyl methacrylate/PDMS macromer - 20,000 mw (10/70/20);
acrylic acid/methyl methacrylate/PDMS macromer - 20,000 mw (40/40/20);
acrylic acid/isopropyl methacrylate/PDMS macromer - 20,000 mw (25/65/15);
acrylic acid/methoxyethyl methacrylate/PDMS macromer 20,000 mw (60/25/15);
acrylic acid/PDMS macromer - 20,000 mw (80/20);
and mixtures thereof.

9. A liquid hair cosmetic composition according to any of Claims 1 to 8 wherein the silicone-containing copolymer is neutralised to a level of from about 0.5% to about 8%, preferably from about 1% to about 6% with organic base and to a level of from about 40% to about 70%, preferably from about 55% to about 65% with inorganic base.

10. A liquid hair cosmetic composition according to any of Claims 1 to 9 wherein the silicone-containing copolymer is neutralised to a total level of from 30% to 95% , preferably from 55% to 75% , more preferably from 60% to 70% .
11. A liquid hair cosmetic composition according to any of Claims 1 to 10 wherein the weight ratio of inorganic base to organic base is in the range of from 1000:1 to about 4:1; preferably from 100:1 to 5:1, more preferably from 50:1 to 6:1.
12. A liquid hair cosmetic composition according to any of Claims 1 to 11 wherein the inorganic base is selected from alkali, alkaline earth and ammonium hydroxides and mixtures thereof, preferably potassium hydroxide or sodium hydroxide.
13. A liquid hair cosmetic composition according to any of Claims 1 to 12 wherein the organic base is selected from amines and amino alcohols and is preferably an amino alcohol selected from 2-amino-2-methyl-1,3-propanediol (AMPD), 2-amino-2-ethyl-1,3-propanediol (AEPD), 2-amino-2-methyl-1-propanol (AMP), 2-amino-1-butanol (AB), monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), monoisopropanolamine (MIPA), diisopropanolamine (DIPA), triisopropanolamine (TIPA) and dimethyl steramine (DMS) and mixtures thereof and is preferably amino methyl propanol.
14. A liquid hair cosmetic composition according to any of Claims 1 to 13 wherein the mixed inorganic/organic base neutralising system comprises potassium hydroxide and amino methyl propanol.
15. A liquid hair cosmetic product comprising a hairspray composition and spray dispenser means for containing and spraying the hairspray composition, and wherein the hairspray composition comprises:

- (a) from about 0.1 % by weight to about 10% by weight (acid basis) of a silicone-containing polycarboxylic acid copolymer having a vinyl polymeric backbone, and having grafted to the backbone a silicone-containing macromer having a weight average molecular weight of from about 1,000 to about 50,000;
- (b) a mixed neutralising system comprising an organic and an inorganic base, wherein the organic base is at a level sufficient to neutralise from about 0.01 % to about 15% of the acid groups on the silicone-containing copolymer while the inorganic base is at a level sufficient to neutralise from about 25% to about 80% , preferably from about 50% to about 70% of the acid groups on the silicone-containing copolymer;
- (c) from 0% to about 10% by weight of water; and
- (d) the balance comprising a carrier suitable for application to hair.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/05245

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :A61K 7/08, 7/48, 7/13

US CL :424/70, 71; 514/781

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 424/70, 71

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 5,104,646 (BOLICH JR. ET AL) 14 April 1992, column 22, lines 15-65, column 23, lines 1-55, column 24, lines 1-25, column 25, lines 20-25, claims.	1-3, 15

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be part of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"G" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

07 SEPTEMBER 1994

Date of mailing of the international search report

21 OCT 1994

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

J. VENKAT

Telephone No. (703) 308-2351

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/05245

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 4-14
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶: A61K 7/06	A1	(11) International Publication Number: WO 95/04518 (43) International Publication Date: 16 February 1995 (16.02.95)
(21) International Application Number: PCT/US94/08031 (22) International Filing Date: 19 July 1994 (19.07.94) (30) Priority Data: 08/102,433 5 August 1993 (05.08.93) US (71) Applicant: THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventors: MIDHA, Sanjeev; 9274 Deercross Parkway, Blue Ash, OH 45236 (US). TORGERSON, Peter, Marte; 4127 U.S. Route 35 NW, Washington Court House, OH 43160 (US). HALL, Christine; 6072 Dryden Avenue, Cincinnati, OH 45213 (US). (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45202 (US).		(81) Designated States: AM, AU, BB, BG, BR, BY, CA, CN, CZ, FI, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LV, MD, MG, MN, MW, NO, NZ, PL, RO, RU, SD, SI, SK, TJ, TT, UA, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: HAIR STYLING COMPOSITIONS CONTAINING A SILICONE GRAFTED POLYMER AND LOW LEVEL OF A VOLATILE HYDROCARBON SOLVENT (57) Abstract Provided hair styling compositions comprising: (a) from about 0.1 % to about 15 %, by weight, of a silicone grafted adhesive polymer, said polymer being characterized by an organic polymeric backbone having silicone macromers grafted to said backbone; (b) from about 0.5 % to about 15 %, by weight, of a hydrocarbon solvent selected from the group consisting of C ₁₀ -C ₁₄ branched chain hydrocarbons, and mixtures thereof; (c) a polar solvent phase comprising from about 80 % to about 98.9 %, by weight of the composition, of a polar solvent selected from the group consisting of water and C ₂ -C ₃ monohydric alcohols, and mixtures thereof, wherein said composition contains no more than about 15 %, by weight, of C ₃ monohydric alcohol; wherein said organic polymer backbone is soluble in said polar solvent phase, and said silicone macromers of said hair setting polymer are soluble in said hydrocarbon solvent and insoluble in said polar solvent. In preferred embodiments, the compositions hereof additionally comprise a plasticizer for the silicone grafted hair setting polymer. Especially preferred plasticizers include acetyl tri-C ₂ -C ₈ alkyl citrates, particularly acetyl triethyl citrate.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

HAIR STYLING COMPOSITIONS CONTAINING A SILICONE GRAFTED
POLYMER AND LOW LEVEL OF A VOLATILE HYDROCARBON
SOLVENT

5

10

TECHNICAL FIELD

The present invention relates to hair styling compositions containing a silicone organic polymer as a hair setting agent. More particularly, the present invention relates to hairs styling compositions containing a silicone grafted organic polymer, having an organic backbone that is soluble either in water, lower alkanol, or a mixture thereof, and further containing an insoluble hydrocarbon solvent.

15

BACKGROUND OF THE INVENTION

The desire to have the hair retain a particular shape is widely held. The most common methodology for accomplishing this is the application of a composition to dampened hair, after shampooing and/or conditioning, or to dry, styled hair. These compositions provide temporary setting benefits and they can be removed by water or by shampooing. The materials used in the compositions to provide the setting benefits have generally been resins and have been applied in the form of mousses, gels, lotions or sprays.

20

25

Many people desire a high level of style retention, or hold, from a hair spray composition. In typical hair sprays, hold is achieved by the use of resins, such as AMPHOMER^R, supplied by National Starch and Chemical Company, and GANTREZ^R SP 225, supplied by GAF. In general, as hair hold for hair spray compositions is increased, the tactile feel of the hair becomes stiffer and hence, less desirable. It is desirable to provide hair spray products which could provide an improved combination of hair hold and hair feel characteristics.

30

Hair sprays have been conventionally formulated with high amounts of monohydric alcohol solvents, such as ethanol and isopropanol, and relatively low amounts of water since the presence of water adversely affects spray quality. However, it is now particularly desirable to formulate hair spray compositions with reduced levels of volatile organic compounds, such as ethanol, isopropanol, and other volatile materials, such as aerosol propellants. One way to do this is to increase the levels of water in the formulations. In doing so, it would be highly desirable to provide reformulated products which overcome the problems conventionally associated with the addition of water to hair spray products. In particular, higher levels of water can negatively impact hair feel.

Recently, it has become known to utilize silicone grafted organic backbone polymers as hair setting agents in hairspray compositions and other hair styling compositions, e.g. hair tonics, lotions, rinses, mousses, etc. Silicone grafted polymers can be used to make hair spray compositions which provide hair setting ability with improved hair feel, e.g., increased softness relative to conventional polymeric hair setting agents.

However, it remains desirable to improve the hair feel performance these silicone grafted polymers can provide at a particular level of hair hold, or conversely, to improve hair hold (after application and drying of such compositions) for a particular level of hair feel performance. It is an object of this invention to provide hair spray compositions, and other aqueous, alcohol, or hydroalcoholic-based hair setting solutions, containing silicone grafted organic backbone polymeric hair setting agents that provide such improved combinations of hair feel/hair hold performance.

It is a further object of this invention to provide hair setting compositions, as described above, that provide both improved hair feel and improved hair hold ability for a particular level of silicone grafted polymer in the composition.

It is yet a further object of this invention to provide compositions that meet the above objects for conventional volatile organic solvent level (conventional VOC) compositions, which typically contain greater than 80% of volatile organic compounds, as well as for reduced volatile

organic solvent level (reduced VOC) compositions, i.e., compositions having 80% or less volatile organic solvents.

These and other benefits as may be apparent from the description below can be obtained by the present invention.

5 The present compositions can comprise, consist of, or consist essentially of any of the required or optional ingredients and/or limitations described herein.

10 All percentages and ratios are calculated on a weight basis unless otherwise indicated. All percentages are calculated based upon the total composition unless otherwise indicated.

All ingredient levels are refer to the active level of that ingredient, and are exclusive of solvents, by-products, or other impurities that may be present in commercially available sources, unless otherwise indicated.

15 SUMMARY OF THE INVENTION

The present invention relates to hair styling compositions comprising:

- 20 (a) from about 0.1% to about 15%, by weight, of a silicone grafted adhesive polymer, said polymer being characterized by an organic polymeric backbone having silicone macromers grafted to said backbone;
- (b) from about 0.5% to about 15%, by weight, of a hydrocarbon solvent selected from the group consisting of C₁₀-C₁₄ branched chain hydrocarbons, and mixtures thereof, having
25 a boiling point of from about 105°C to about 260°C;
- (c) a polar solvent phase comprising from about 80% to about 98.9%, by weight of the composition, of a polar solvent selected from the group consisting of water and C₂-C₃ monohydric alcohols, and mixtures thereof, wherein said
30 composition contains no more than about 15%, by weight, of C₃ monohydric alcohol;

wherein said organic polymer backbone is soluble in said polar solvent phase, and said silicone macromers of said hair setting polymer are soluble in said hydrocarbon solvent and insoluble in said polar solvent.

35 In preferred embodiments, the compositions hereof additionally comprise a plasticizer for the silicone grafted hair setting polymer.

Especially preferred plasticizers include acetyl tri-C₂-C₈ alkyl citrates, particularly acetyl triethyl citrate.

DETAILED DESCRIPTION OF THE INVENTION

The essential components of the present invention are described below. Also included is a nonexclusive description of various optional and preferred components useful in embodiments of the present invention.

Silicone Grafted Adhesive Polymer

The compositions of the present invention essentially comprise a silicone grafted adhesive polymer as a hair setting agent. The compositions hereof will generally comprise from about 0.1% to about 15%, preferably from 0.5% to about 8%, more preferably from about 1% to about 8%, by weight of the composition, of the silicone grafted polymer. It is not intended to exclude the use of higher or lower levels of the polymers, as long as an effective amount is used to provide adhesive or film-forming properties to the composition and the composition can be formulated and effectively applied for its intended purpose. By adhesive polymer what is meant is that when applied as a solution to a surface and dried, the polymer forms a film. Such a film will have adhesive and cohesive strength, as is understood by those skilled in the art.

The silicone grafted polymers are characterized by polysiloxane moieties covalently bonded to and pendant from a polymeric carbon-based backbone. The backbone will preferably be a carbon chain derived from polymerization of ethylenically unsaturated monomers, but can also be, cellulosic chains or other carbohydrate-derived polymeric chains to which polysiloxane moieties are pendant. The backbone can also include ether groups, i.e., C-O-C. The polysiloxane moieties can be substituted on the polymer or can be made by co-polymerization of polysiloxane-containing polymerizable monomers (e.g. ethylenically unsaturated monomers, ethers, and/or epoxides) with non-polysiloxane-containing polymerizable monomers.

The polysiloxane-grafted polymer should have a weight average molecular weight of at least about 20,000. There is no upper limit for molecular weight except that which limits applicability of the invention for practical reasons, such as processing, aesthetic characteristics, formulateability, etc. In general, the weight average molecular weight will be less than about 10,000,000, more generally less than about

5,000,000, and typically less than about 3,000,000. Preferably, the weight average molecular weight will be between about 50,000 and about 2,000,000, more preferably between about 75,000 and about 1,000,000, most preferably between about 100,000 and about 750,000.

5 Preferably, the grafted-polymers hereof when dried to form a film have a Tg or Tm of at least about -20°C, preferably at least about 20°C, so that they are not unduly sticky, or "tacky" to the touch. As used herein, the abbreviation "Tg" refers to the glass transition temperature of the non-polysiloxane backbone of the polymer, and the abbreviation "Tm" refers to the crystalline melting point of the non-siloxane backbone, if such a transition exists for a given polymer. Preferably, both the Tg and the Tm, if any, are above about -20°C, more preferably above about 20°C.

15 The silicone grafted polymers for the compositions of the present invention include "silicone-containing" (or "polysiloxane-containing") monomers, which form the silicone macromer pendant from the backbone, and non-silicone-containing monomers, which form the organic backbone of the polymer.

20 The silicone grafted polymers should satisfy the following four criteria:

- (1) when dried the polymer phase-separates into a discontinuous phase which includes the polysiloxane portion and a continuous phase which includes the non-polysiloxane portion;
- 25 (2) the polysiloxane portion is covalently bonded to the non-polysiloxane portion; and
- (3) the molecular weight of the polysiloxane portion is at least about 500; and

30 When used in a composition, such as a personal care composition for application to the hair or skin, the non-polysiloxane portion should permit the polymer to deposit on the intended surface, such as hair or skin.

35 It is believed that the phase separation property provides a specific orientation of the polymer which results in the desired combination of tactile feel, and film-forming or adhesive benefits. The phase-separating nature of the compositions of the present invention may be determined as follows:

The polymer is cast as a solid film out of a solvent (i.e., a solvent which dissolves both the backbone and the polysiloxane-graft portions). This film is then sectioned and examined by transmission electron microscopy. Microphase separation is demonstrated by the observation of inclusions in the continuous phase. These inclusions should have the proper size to match the size of the silicone chain (typically a few hundred nm or less) and the proper density to match the amount of silicone present. This behavior is well documented in the literature for polymers with this structure (see, for example, S. D. Smith, Ph.D. Thesis, University of Virginia, 1987, and references cited therein, said thesis incorporated by reference herein).

A second method for determining phase-separating characteristics involves examining the enrichment of the concentration of silicone at the surface of a polymer film relative to the concentration in the bulk polymer. Since the silicone prefers the low energy air interface, it preferentially orients on the polymer surface. This produces a surface with the silicone oriented at the surface of the film. This can be demonstrated experimentally by ESCA (electron spectroscopy for chemical analysis) of the dried film surface. Such an analysis shows a high level of silicone and a greatly reduced level of backbone polymer when the film surface is analyzed. (Surface here means the first few tens of Angstroms of film thickness.) By varying the angle of the interrogating beam the surface can be analyzed to varying depths.

A third method for determining phase-separating characteristics is via Scanning Electron Microscopy (SEM), to examine the topographical morphology of dried film of the silicone grafted polymer. SEM can be used to demonstrate microphase separation at the surface of the polymer film by the observation of hemi-spherical discontinuities (typically hemi-spherical or hemi-conical) formed by the silicone macromer component grafted on the polymer backbone of the silicone grafter polymer.

The preferred silicone grafted polymers comprise an organic backbone preferably a carbon backbone derived from ethylenically unsaturated monomers, such as a vinyl polymeric backbone, and a polysiloxane macromer (especially preferred are polydialkylsiloxane, most preferably polydimethylsiloxane) grafted to the backbone. The polysiloxane macromer should have a weight average molecular weight of at least about 500, preferably from about 1,000 to about 100,000, more

preferably from about 2,000 to about 50,000, most preferably about 5,000 to about 20,000. Organic backbones contemplated include those that are derived from polymerizable, ethylenically unsaturated monomers, including vinyl monomers, and other condensation monomers (e.g., those that polymerize to form polyamides and polyesters), ring-opening monomers (e.g., ethyl oxazoline and caprolactone), etc. Also contemplated are backbones based on cellulosic chains, ether-containing backbones, etc.

Examples of useful polymers and how they are made are described in detail in U.S. Patent 4,693,935, Mazurek, issued September 15, 1987, U.S. Patent 4,728,571, Clemens et al., issued March 1, 1988, both of which are incorporated herein by reference.

Suitable silicone grafted polymers are also disclosed in EPO Application 90307528.1, published as EPO Application 0 408 311 A2 on January 11, 1991, Hayama, et al., U.S. Patent 5,061,481, issued October 29, 1991, Suzuki et al., U.S. Patent 5,106,609, Bolich et al., issued April 21, 1992, U.S. Patent 5,100,658, Bolich et al., issued March 31, 1992, U.S. Patent 5,100,657, Ansher-Jackson, et al., issued March 31, 1992, U.S. Patent 5,104,646, Bolich et al., issued April 14, 1992, U.S. Serial No. 07/758,319, Bolich et al, filed August 27, 1991, and U.S. Serial No. 07/758,320, Torgerson et al., filed August 27, 1991, all of which are incorporated by reference herein.

The preferred silicone grafted polymers are comprised of monomer units derived from: at least one free radically polymerizable ethylenically unsaturated monomer or monomers and at least one free radically polymerizable polysiloxane-containing ethylenically unsaturated monomer or monomers.

The silicone grafted polymers hereof generally comprise from about 1% to about 50%, by weight, of polysiloxane-containing monomer units, i.e., monomer units polysiloxane-containing monomers (referred to herein as "C" monomers), and from about 50% to about 99% by weight, of non-polysiloxane-containing monomers.

The non-polysiloxane-containing monomer units can be derived from polar, or hydrophilic, monomers, "A" monomers, or mixtures of polar hydrophilic monomers and low polarity, or hydrophobic, "B" monomers.

Hydrophobic monomers means monomers which form substantially water insoluble homopolymers. Hydrophilic monomers

means monomers which do not form substantially water insoluble homopolymers. Substantially water soluble shall refer to monomers that form homopolymers that are soluble in distilled (or equivalent) water, at 25°C, at a concentration of 0.2% by weight, and are preferably soluble at 1.0% by weight. Substantially water insoluble shall refer to monomers that form homopolymers that are not soluble in distilled (or equivalent) water, at 25°C, at a concentration of 0.2% by weight, and preferably not soluble at 0.1% by weight. The weight average molecular weight for purposes of determining substantial water solubility or insolubility shall be about 100,000, although solubility at higher molecular weight shall also be indicative of solubility at about 100,000.

The particular relative amounts of A, B, and C monomers can vary as long as the polymer backbone is soluble in the polar solvent hereof and the silicone grafted copolymer exhibits phase separation when dried.

Representative examples of A monomers include acrylic acid, methacrylic acid, N,N-dimethylacrylamide, dimethyl aminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, methacrylamide, N-t-butyl acrylamide, maleic acid, maleic anhydride and its half esters, crotonic acid, itaconic acid, acrylamide, acrylate alcohols, hydroxyethyl methacrylate, diallyldimethyl ammonium chloride, vinyl pyrrolidone, vinyl ethers (such as methyl vinyl ether), maleimides, vinyl pyridine, vinyl imidazole, other polar vinyl heterocyclics, styrene sulfonate, allyl alcohol, vinyl alcohol (such as that produced by the hydrolysis of vinyl acetate after polymerization), vinyl caprolactam, salts of any acids and amines listed above, and mixtures thereof. Preferred A monomers include acrylic acid, N,N-dimethyl acrylamide, dimethylaminoethyl methacrylate, quaternized dimethyl aminoethyl methacrylate, vinyl pyrrolidone, salts of acids and amines listed above, and mixtures thereof.

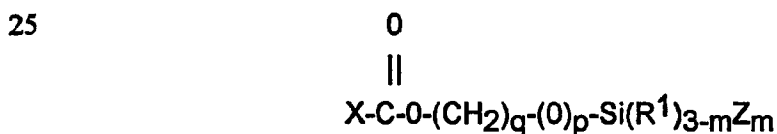
Representative examples of B monomers are acrylic or methacrylic acid esters of C₁-C₁₈ alcohols, such as methanol, ethanol, methoxy ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 1-methyl-1-butanol, 3-methyl-1-butanol, 1-methyl-1-pentanol, 2-methyl-1-pentanol, 3-methyl-1-pentanol, t-butanol(2-methyl-2-propanol), cyclohexanol, neodecanol, 2-ethyl-1-butanol, 3-heptanol, benzyl alcohol, 2-octanol, 6-methyl-1-heptanol, 2-ethyl-1-hexanol, 3,5-dimethyl-1-

hexanol, 3,5,5-tri methyl-1-hexanol, 1-decanol, 1-dodecanol, 1-hexadecanol, 1-octa decanol, and the like, the alcohols having from about 1-18 carbon atoms with the number of carbon atoms preferably being from about 1-12; styrene; polystyrene macromer; vinyl acetate; vinyl chloride; vinylidene chloride; vinyl propionate; alpha-methylstyrene; t-butylstyrene; butadiene; cyclohexadiene; ethylene; propylene; vinyl toluene; and mixtures thereof. Preferred B monomers include n-butyl methacrylate, isobutyl methacrylate, t-butyl acrylate, t-butyl methacrylate, 2-ethylhexyl methacrylate, methyl methacrylate, and mixtures thereof. Most preferably, B is selected from t-butyl acrylate, t-butyl methacrylate, and mixtures thereof.

Polymerizable polysiloxane-containing monomers (C monomer) are exemplified by the general formula:



wherein X is an ethylenically unsaturated group copolymerizable with the A and B monomers, such as a vinyl group; Y is a divalent linking group; R is a hydrogen, hydroxyl, lower alkyl (e.g. C₁-C₄), aryl, alkaryl, alkoxy, or alkylamino; Z is a monovalent siloxane polymeric moiety having a number average molecular weight of at least about 500, is essentially unreactive under copolymerization conditions, and is pendant from the vinyl polymeric backbone described above; n is 0 or 1; and m is an integer from 1 to 3. C has a weight average molecular weight as described above. Preferably, the C monomer has a formula selected from the following group:

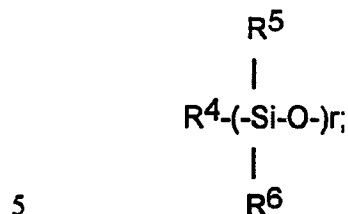


In this structure, m is 1, 2 or 3 (preferably m = 1); p is 0 or 1; q is an integer from 2 to 6; R¹ is hydrogen, hydroxyl, lower alkyl, alkoxy, alkylamino, aryl, or alkaryl (preferably R¹ is alkyl); X is



R² is hydrogen or -COOH (preferably R² is hydrogen); R³ is hydrogen, methyl or -CH₂COOH (preferably R³ is methyl); Z is

10



5

10 R^4 , R^5 , and R^6 independently are lower alkyl, alkoxy, alkylamino, aryl, aralkyl, hydrogen or hydroxyl (preferably R^4 , R^5 , and R^6 are alkyls); and r is an integer of about 5 or higher, preferably about 10 to about 1500 (most preferably r is from about 100 to about 250). Most preferably, R^4 , R^5 , and R^6 are methyl, $p=0$, and $q=3$.

15 In general, the silicone grafted polymer will preferably comprise from about 50% to about 99%, more preferably from about 60% to about 98%, most preferably from about 75% to about 95%, by weight of the polymer, of non-silicone macromer-containing monomer units, e.g. the total A and B monomer units, and from about 1% to about 50%, preferably from about 1% to about 40%, more preferably from about 2% to about 25%, of silicone macromer-containing monomer units, e.g. the C monomer units. The level of A monomer units can be from about 1% to about 99%, preferably from about 5% to about 80%, more preferably from about 10% to about 50%, most preferably from about 15% to about 40%; the level of B monomer units, can be from 0% to about 99%, preferably from about 1% to about 90%, more preferably from about 5% to about 85%, most preferably from about 15% to about 80%; and the level of C monomer units, from about 1% to about 50%, preferably from about 1% to about 40%, more preferably from about 2% to about 25%.

25 The composition of any particular silicone grafted polymer will help determine its formulational properties. By appropriate selection and combination of particular A, B and C components, the silicone grafted polymer can be optimized for inclusion in specific vehicles. The backbone of the silicone grafted polymer included in the compositions hereof must be soluble in the polar solvent, which is hereinafter referred to as the silicone grafted polymer, as a whole, being soluble in the polar solvent. This is determined according to whether the polymer can stay in solution or precipitates out of solution at 25°C at the concentration present in the composition or whether the range of concentrations for silicone grafted polymer described herein. It is well within the skill of one

35

in the art to select monomers for incorporation into the polymers for formulateability and solubility in selected polar solvent systems.

Exemplary silicone grafted polymers for use in the present invention include the following:

- 5 (i) acrylic acid/n-butylmethacrylate/polydimethylsiloxane (PDMS) macromer 20,000 molecular weight macromer
- (ii) dimethylaminoethyl methacrylate/isobutyl methacrylate/2-ethylhexyl-methacrylate/PDMS macromer-20,000 molecular weight macromer
- 10 (iii) t-butylacrylate/acrylic acid/PDMS macromer-10,000 molecular weight macromer
- (iv) t-butylacrylate/acrylic acid/PDMS macromer-20,000 molecular weight macromer

The silicone grafted polymers can be synthesized by free radical
15 polymerization of the polysiloxane-containing monomers with the non-polysiloxane-containing monomers. The general principles of free radical polymerization methods are well understood. See, for example, Odian, "Principles of Polymerization", 2nd edition, John Wiley & Sons, 1981, pp. 179-318. The desired monomers are all placed in a reactor,
20 along with a sufficient amount of a mutual solvent so that when the reaction is complete the viscosity of the reaction is reasonable. Typical monomer loadings are from about 20% to about 50%. Undesired terminators, especially oxygen, are removed as needed. This is done by evacuation or by purging with an inert gas, such as argon or nitrogen.
25 The initiator is introduced and the reaction brought to the temperature needed for initiation to occur, assuming thermal initiators are used. Alternatively, redox or radiation initiation can be used. The polymerization is allowed to proceed as long as needed for a high level of conversion to be achieved, typically from a few hours to a few days.
30 The solvent is then removed, usually by evaporation or by precipitating the polymer by addition of a nonsolvent. The polymer can be further purified, as desired.

In particular the silicone grafted polymers can be purified by removing unreacted silicone-containing monomer and silicone
35 macromer-grafted polymer with viscosities at 25°C of about 10,000,000 centistokes and less. This can be done, for the example, by hexane extraction. After drying the resin from its reaction solvent hexane

extraction of the reaction product can be performed by adding an excess of hexane to the reaction product and heating to near the Tg of the non-silicone portion of the polymer. The mixture is held at this temperature with stirring for about 30 minutes and cooled to room
5 temperature. The hexane is removed by vacuum suction. Two more hexane extraction cycles are preferably conducted in the same manner as above. After the third cycle, residual hexane remaining with the product is removed by distillation and vacuum drying.

As an alternative to a batch reaction, the silicone grafted polymer
10 can be made by a semi-continuous or continuous process. In the semi-continuous process, two or more additions of monomers is made during the polymerization reaction. This is advantageous when the polymer is made of several monomers which react during the polymerization at different rates. The proportions of monomers added to the reaction at
15 the separate points of addition can be adjusted by one of ordinary skill in the art such that the polymers of the final product have a more uniform structure. In other words, the polymers of the final product will have a more consistent monomer content distribution for each of the monomer types charged to the reaction. Typically, the silicone macromer-
20 combining monomers, the "C" monomers as described above, well react more slowly than the non-silicone macromer-containing monomers. To compensate for this, for example, more consistent distribution of C monomer can be obtained by adding all the C monomer and half of the A and B monomers in the first addition of monomers to the reaction, and
25 the rest of the A and B monomers in a second addition.

As is known in the art, polymers which have acidic functionalities, such as carboxyl groups, are usually used in at least partially neutralized form to promote solubility/dispersibility of the polymer. In addition, use of the neutralized form aids in the ability of the hair care compositions to be
30 removed from the hair by shampooing. In general, it is preferred that from about 10% to 100%, more preferably from about 20% to about 90%, even more preferably from about 40% to about 85%, of the acidic monomers of the polymer be neutralized.

Any conventionally used base, organic or metallic, may be used
35 for neutralization of the polymers. Metallic bases are particularly useful in the present compositions. Hydroxides, where the cation is an alkali

metal or an alkaline earth metal, are suitable neutralizers for use in the present hair spray compositions.

Preferred neutralizing agents for use in hair spray compositions of the present invention are potassium hydroxide and sodium hydroxide.

5 Examples of other suitable neutralizing agents which may be included in the hair spray compositions of the present invention include amines, especially amino alcohols such as 2-amino-2-methyl-1,3-propanediol (AMPD), 2-amine-2-ethyl-1,3-propanediol (AEPD), 2-amino-2-methyl-1-propanol (AMP), 2-amino-1-butanol (AB),
10 monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), monoisopropanolamine (MIPA), diisopropanol-amine (DIPA), tri-isopropanolamine (TIPA) and dimethyl steramine (DMS). Particularly useful neutralizing agents are mixtures of amines and metallic bases.

15 Polymers having basic functionalities, e.g., amino groups, are preferably at least partially neutralized with an acid, e.g., hydrogen chloride.

20 Solubility of the silicone grafted polymer, as described above, should be determined after neutralization, if any, as well as after addition of other ingredients that may be included in the polar solvent phase, such as surfactants, solubilizers, etc.

Polar Solvent Phase

25 The liquid care compositions of the present invention also include a polar solvent phase as a liquid vehicle for the silicone grafted polymer. The polar solvent phases comprise one or more polar solvents that are present in the hair care compositions at a level of from about 80% to about 98.9%, preferably from about 85% to about 98%, more preferably from about 90% to about 95% of the total composition.

30 The polar solvents essential to the present compositions are selected from the group consisting of water C₂-C₃ monohydric alkanols, and mixtures thereof. If present, C₃ alkanols, such as isopropanol, should be used at levels no greater than about 15% by weight of the composition, preferably no greater than about 12%, more preferably no greater than about 10%. High levels of C₃ monohydric alcohols are undesirable in the present compositions due to potential odor issues they
35 can create. Preferred polar solvent phases contain water, ethanol, or mixtures thereof.

Where water and alcohol mixtures are used, for instance, water-ethanol or water-isopropanol-ethanol, the water content of the compositions is generally in the range of from about 0.5% to about 99%, preferably from about 5% to about 50% by weight of the total composition. In such mixtures, the alcohol solvents are generally present in the range of from 0.5% to about 99%, preferably from about 50% to about 95%, by weight of the total composition.

In yet another aspect of this invention are provided hair styling products, such as hair spray compositions, which contain reduced levels of volatile organic solvents. A reduced volatile organic solvent hair spray composition of the present invention contains no more than 80% volatile organic solvents (which include, for example, alkanols but not water). As used herein, volatile organic solvents means solvents which have at least one carbon atom and exhibit a vapor pressure of greater than 0.1 mm Hg at 20°C.

In the reduced volatile organic solvent hair styling products hereof, the compositions generally comprise at least 10%, by weight, of water. It is also specifically contemplated that they may contain at least about 11%, 12%, 13%, 14%, 15%, or more water.

The reduced volatile organic solvent compositions hereof will comprise up to about 90%, preferably up to about 70%, more preferably up to about 60% even more preferably no more than about 50%, water; and from about 10% to about 80%, preferably from about 20% to about 80%, more preferably from about 40% to about 80%, of volatile organic solvent. It is also contemplated that the compositions can be limited to containing no more than about 75%, 65%, 55%, or other levels of volatile organic solvents.

Nonpolar, Branched Chain Hydrocarbon

The compositions hereof contain as an essential element a volatile, nonpolar, branched chain hydrocarbon, which acts as a solvent for the silicone portion of the silicone grafted copolymer and is safe for topical application to the skin and hair. The branched chain hydrocarbon solvent hereof is present at a level of from about 0.5% to about 15%, preferably from about 1% to about 10%, more preferably from about 2% to about 8%, by weight of the composition.

The branched chain hydrocarbon solvent is characterized by a boiling point of at least about 105°C, preferably at least about 110°C,

more preferably at least about 125°C, most preferably at least about 150 °C . The boiling point is also generally about 260°C or less, preferably about 200°C or less. The hydrocarbon chosen should also be safe for topical application to the hair and skin.

5 The branched chain hydrocarbon solvents are selected from the group consisting of C₁₀-C₁₄ branched chain hydrocarbons, and mixtures thereof, preferably C₁₁-C₁₃ branched chain hydrocarbons, more preferably C₁₂ branched chain hydrocarbons. Saturated hydrocarbons are preferred, although it isn't necessarily intended to exclude
10 unsaturated hydrocarbons.

 Examples of suitable nonpolar solvents include isoparaffins of the above chain sizes. Isoparaffins are commercially available from Exxon Chemical Co. Examples include IsoparTM G (C₁₀-C₁₁ isoparaffins), IsoparTM H and K (C₁₁-C₁₂ isoparaffins), and IsoparTM L (C₁₁-C₁₃
15 isoparaffins). The most preferred nonpolar solvent are C₁₂ branched chain hydrocarbons, especially isododecane. Isododecane is commercially available from Preperse, Inc. (South Plainfield, NJ, USA) as PermethylTM 99A.

 The silicone macromer portion of the silicone grafted polymer is
20 soluble in the nonpolar hydrocarbon solvent in the present compositions. This can be easily determined by verifying whether a silicone macromer of the same composition and molecular weight as that grafted to the silicone grafted polymer is soluble in the nonpolar hydrocarbon solvent. In general, the macromer should be soluble at 25°C at a concentration of
25 0.1% by weight of the hydrocarbon solvent, preferably at 1%, more preferably at 5%, most preferably at 15%.

 The nonpolar hydrocarbon solvent, however, is insoluble in the polar solvent of the composition. This is determined in the absence of the silicone grafted polymer, or other emulsifying agents, and can easily
30 be verified by observing whether the polar and nonpolar solvents form separate phases after being mixed together.

 Without intending to be necessarily limited by any particular theory, it is believed that the nonpolar hydrocarbon solvent solubilizes the silicone macromer portion of the silicone grafted polymer. This is
35 believed to aid in obtaining a smoother polymer film upon drying. Since the hydrocarbon solvent is less volatile than the polar solvent phase, the hydrocarbon solvent maintains the silicone portions in solubilized form

for a relatively long period as the composition dries, thus minimizing aggregation of the silicone portions and, therefore, allowing the polymer to dry as a smoother film.

Plasticizer

5 The compositions hereof can optionally contain a plasticizer for the silicone grafted polymer. Any plasticizer suitable for use in hair care products or for topical application to the hair or skin can be used. A wide variety of plasticizers are known in the art. These include glycerin, diisobutyl adipate, butyl stearate, and propylene glycol. Plasticizers are
10 typically used at levels of from about 0.01% to about 10%, by weight of the composition, preferably from about 0.05% to about 3%, more preferably from about 0.05% to about 1%.

15 In a highly preferred embodiment hereof, surprising improvements in hair hold performance can be obtained when the present compositions have included therein certain plasticizers selected from the group consisting of acetyl tri-C₂-C₈ alkyl citrates, such as acetyl triethyl citrate. Other suitable examples include the tri-propyl, -butyl, -pentyl, etc., analogues of acetyl triethyl citrate.

20 Whereas it has been found that plasticizers of this type result in a brittle, gritty film of the silicone grafted polymer when formed from a composition not including the hydrocarbon solvent of the present invention, the use of the acetyl tri-alkyl citrate in the presence of the hydrocarbon solvent in the present compositions can provide improved hair hold relative to the citrate-free composition, without causing the hair
25 to feel brittle or gritty, and while also allowing the hair to exhibit improved softness and comb-ability relative to a citrate plasticizer-containing composition that does not contain the nonpolar hydrocarbon solvent hereof.

30 The acetyl tri-alkyl citrate plasticizer hereof is generally used at a level of from about 0.025% to about 2%, preferably from about 0.05% to about 1%, by weight of the composition. Preferably, the weight ratio of silicone grafted polymer to the acetyl tri-alkyl citrate is from about 1:1 to about 40:1, preferably from about 10:1 to about 30:1, more preferably from about 15:1 to about 25:1.

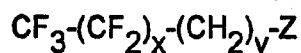
35 Optional Ingredients

The present compositions can contain a wide variety of optional ingredients, including among them any of the types of ingredients known

in the art for use in hair setting compositions, especially hair spray compositions and hair setting tonics. These ingredients include, but are not limited to, surfactants (including fluorinated surfactants and silicone copolyols, and silicone tonic strength modifiers, non-silicone grafted film-forming polymers, propellants, hair conditioning agents (e.g., silicone fluids, fatty esters, fatty alcohols, long chain hydrocarbons, cationic surfactants, etc.)

Fluorosurfactants

Fluorosurfactants useful in the present compositions include perfluorinated compounds which can be represented by the formula



where Z is a water solubilizing group of either organic or inorganic character, x is an integer which is generally from 2 to 17, particularly from 7 to 11, and y is an integer from 0 to 4, and said compounds may be cationic, anionic, amphoteric or zwitterionic, depending upon the nature of the grouping or groupings encompassed by Z. The Z groups may be or may comprise sulfate, sulfonate, carboxylate, amine salt, quaternary ammonium, phosphate, phosphonate, and combinations thereof. The perfluorinated compounds are known in the art. These compounds are described in U.S. Patent 4,176,176, Cella et al., issued November 27, 1979; U.S. Patent 3,993,745, Cella et al., issued November 23, 1976, and U.S. Patent 3,993,744, Cella et al., issued November 23, 1976, each being incorporated herein by reference.

Suitable anionic fluorosurfactants can have anionic moieties which include carboxylates, sulfates, sulfonates, phosphonates and phosphates or any combination thereof. Counterions therefore can include sodium, NH_4 , magnesium, potassium, tri-ethanolamine, di-ethanolamine, and similar moieties. Suitable cationic fluorosurfactants can have cationic moieties which include quaternary ammonium compounds where the counterions can be chloride or any other halide, methosulfate, ethosulfate, phosphate, acetate, and other similar moieties. Also, suitable cationic fluorosurfactants can have cationic moieties which include primary, secondary and tertiary amine salts of acids such as hydrochloric, lactic, phosphoric, sulfuric and other similar acids.

Also suitable for use are amphoteric fluorosurfactants, such as Fluorad FC-100® supplied by 3M; and the experimental amphoteric

fluorosurfactant L-12231 supplied by 3M; and also include zwitterionic fluorosurfactants such as those conforming to the formula $R_f\text{CH}_2\text{CH}(\text{OCOCH}_3)\text{CH}_2\text{N}^+(\text{CH}_3)_2\text{CH}_2\text{CO}_2^-$ wherein $R_f=\text{F}(\text{CF}_2\text{CF}_2)_3-8$ such as Zonyl FSK® supplied by DuPont.

- 5 Fluorosurfactant, are typically used at levels of from about 0.01% to about 2%, preferably from about 0.01% to about 1.5%. More preferably from about 0.02% to about 1%.

Non-fluorinated Surfactants

- 10 Optionally, the hair spray compositions can contain one or more non-fluorinated surfactant. Generally, if used such non-fluorinated surfactants will be used at a total level of from about 0.01% to about 2%, preferably from about 0.01% to about 1.5% and more preferably from about 0.01% to about 1%, by weight of the composition.

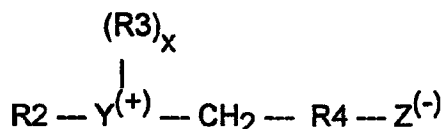
- 15 A wide variety of non-fluorinated surfactants can be used, including anionic, cationic, amphoteric, and zwitterionic surfactants.

- 20 Anionic surfactants include, for example: alkyl and alkenyl sulfates; alkyl and alkenyl ethoxylated sulfates; (preferably having an average degree of ethoxylation of 1 to 10), succinamate surfactants, such as alkylsulfosuccinamates and dialkyl esters of sulfosuccinic acid; neutralized fatty acid esters of isethionic acid; and alkyl and alkenyl sulfonates, including, for example, olefin sulfonates and beta-alkoxy alkane sulfonates. Preferred are alkyl and alkenyl sulfates and alkyl and alkenyl ethoxylated sulfates such as the sodium and ammonium salts of $\text{C}_{12}\text{-C}_{18}$ sulfates and ethoxylated sulfates with a degree of ethoxylation of from 1 to about 6, preferably from 1 to about 4, e.g., lauryl sulfate and laureth (3.0) sulfate.

- 30 Amphoteric surfactants include those which can be broadly described as derivatives of aliphatic secondary and tertiary amines in which the aliphatic radical can be straight chain or branched and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. Examples of compounds falling within this definition are sodium 3-dodecylaminopropionate, N-alkyltaurines such as the one prepared by reacting dodecylamine with sodium isethionate according to the teaching of U.S. Patent 2,658,072, N-higher alkyl aspartic acids such as those produced according to the teaching of U.S. Patent 2,438,091, and the products sold under the trade name "Miranol" and described in U.S. Patent

2,528,378. Others include alkyl, preferably C_6-C_{22} and most preferably C_8-C_{12} , amphoglycinates; alkyl, preferably C_6-C_{22} and most preferably C_8-C_{12} , amphopropionates; and mixtures thereof.

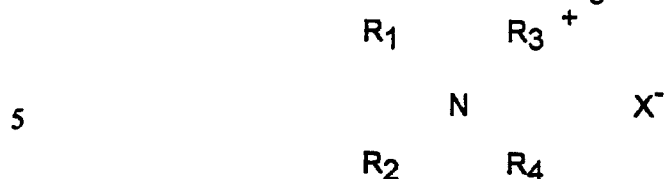
Suitable zwitterionic surfactants for use in the present compositions can be exemplified by those which can be broadly described as derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium compounds, in which the aliphatic radicals can be straight chain or branched, and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms and one contains an anionic water-solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. A general formula for these compounds is:



wherein R2 contains an alkyl, alkenyl, or hydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to 1 glyceryl moiety; Y is selected from the group consisting of nitrogen, phosphorus, and sulfur atoms; R3 is an alkyl or monohydroxyalkyl group containing 1 to about 3 carbon atoms; x is 1 when Y is sulfur or phosphorus, 1 or 2 when Y is nitrogen; R4 is an alkylene or hydroxyalkylene of from 1 to about 4 carbon atoms and Z is a radical selected from the group consisting of carboxylate, sulfonate, sulfate, phosphonate, and phosphate groups. Classes of zwitterionics include alkyl amino sulfonates, alkyl betaines, and alkyl amido betaines.

Cationic surfactants useful in compositions of the present invention contain amino or quaternary ammonium hydrophilic moieties which are positively charged when dissolved in the aqueous composition of the present invention. Cationic surfactants among those useful herein are disclosed in the following documents, all incorporated by reference herein: M. C. Publishing Co., **McCutcheon's, Detergents & Emulsifiers**, (North American edition 1979); Schwartz, et al., **Surface Active Agents, Their Chemistry and Technology**, New York: Interscience Publishers, 1949; U.S. Pat. No. 3,155,591, Hilfer, issued Nov. 3, 1964; U.S. Pat. No. 3,929,678, Laughlin, et al., issued Dec. 30, 1975; U.S. Pat. No. 3,959,461, Bailey, et al., issued May 25, 1976; and U.S. Pat. No. 4,387,090, Bolich, Jr., issued June 7, 1983.

Among the quaternary ammonium-containing cationic surfactant materials useful herein are those of the general formula:



wherein R₁ is an aliphatic group of from 1 to 22 carbon atoms, or an aromatic, aryl or alkylaryl group having from 12 to 22 carbon atoms; R₂ is an aliphatic group having from 1 to 22 carbon atoms; R₃ and R₄ are each alkyl groups having from 1 to 3 carbon atoms, and X is an anion selected from halogen, acetate, phosphate, nitrate and alkylsulfate radicals. The aliphatic groups may contain, in addition to carbon and hydrogen atoms, ether linkages, and other groups such as amido groups. Other quaternary ammonium salts useful herein are diquaternary ammonium salts.

Salts of primary, secondary and tertiary fatty amines are also suitable cationic surfactants for use herein. The alkyl groups of such amines preferably have from 12 to 22 carbon atoms, and may be substituted or unsubstituted. Secondary and tertiary amines are preferred, tertiary amines are particularly preferred. Such amines, useful herein, include stearamido propyl dimethyl amine, diethyl amino ethyl stearamide, dimethyl stearamine, dimethyl soyamine, soyamine, myristyl amine, tridecyl amine, ethyl stearylamine, N-tallowpropane diamine, ethoxylated (5 moles E.O.) stearylamine, dihydroxy ethyl stearylamine, and arachidylbehenylamine. Cationic amine surfactants included among those useful in the present invention are disclosed in U.S. Pat. No. 4,275,055, Nachtigal, et al., issued June 23, 1981 (incorporated by reference herein).

Suitable cationic surfactant salts include the halogen, acetate, phosphate, nitrate, citrate, lactate and alkyl sulfate salts.

Nonionic surfactants can also be included in the compositions hereof. Preferably, the nonionic surfactants have an average HLB (Hydrophile-Lipophile Balance) of less than or equal to about 7.

Methods of determining HLB are well known in the art and any of such methods may be used for HLB determination. A description of the HLB System and methods for HLB determination are described in "The

HLB System: a time saving guide to emulsifier selection, " ICI Americas Inc.; Wilmington, Delaware; 1976.

Nonionic surfactants include polyethylene oxide condensates of alkyl phenols (preferably C₆-C₁₂ alkyl, with a degree of ethoxylation of about 1 to about 6), condensation products of ethylene oxide with the reaction product of propylene oxide and ethylene diamine, condensation products of aliphatic alcohols with ethylene oxide, long chain (i.e., typically C₁₂-C₂₂) tertiary amine oxides, long chain tertiary phosphine oxides, dialkyl sulfoxides containing one long chain alkyl or hydroxy alkyl radical and one short chain (preferably C₁-C₃) radical, silicone copolyols, and C₁-C₄ alkanol amides of acids having a C₈-C₂₂ acyl moiety.

Ionic Strength Modifier System

Optionally, the compositions of the present invention can contain an effective amount of a non-surface active ionic strength modifier system for reducing the viscosity of the hair spray composition. When used, the ionic strength modifiers will be present in the present compositions at a level of at least about 0.01%, by weight of the composition. The upper limit is dependent upon the maximum amount of the ionic strength modifiers that can be present in the particular compositions hereof such that the hair setting resin remains solubilized or dispersed. As will be understood by those skilled in the art, as the ionic strength of the composition is increased, the resin will eventually fall out of solution, or otherwise no longer remain solubilized or dispersed in the polar liquid carrier. The upper limit of the ionic strength modifier system level will vary depending upon the particular ionic strength modifiers, liquid vehicle, resin, and other ingredients present in the composition. Thus, for example, the maximum amount of the ionic strength modifiers that can be used will tend to be lower for compositions with liquid vehicles containing less water, compared to compositions with more water. Generally, the compositions will comprise about 4%, by weight, or less of the ionic strength modifiers, more generally about 2% or less, and typically about 1% or less. Preferably, the compositions hereof will comprise from about 0.01% to about 0.5%, more preferably from about 0.01% to about 0.1%, of the ionic strength modifier system.

The ionic strength modifier system comprises a mixture of monomeric cations and anions. The ions of the ionic strength modifier

system hereof are non-surface active, i.e. they do not significantly reduce surface tension. For purposes hereof, non-surface active shall mean the ions, which at a 0.5% aqueous solution concentration, reduce surface tension by no more than 5.0 dynes/cm². Generally, the ions of the ionic strength modifier system hereof will be characterized by having, at maximum, four or less carbon atoms per charge, preferably two or less carbon atoms, in any aliphatic chain or straight or branched chain organic heterochain.

The ionic strength modifier system comprises monomeric ions of the type which are products of acid-base reactions. Thus, basic and acidic ions OH⁻ and H⁺ do not constitute part of the ionic strength modifier system hereof, although they may be present in the composition. The ions hereof are incorporated into the composition in a form such that they can exist in the composition as free ions, i.e., in dissociated form. It is not necessary that all of the ions added exist in the composition as free ions, but must be at least partially soluble or dissociated in the composition. The ionic strength modifiers can be incorporated into the hair styling compositions, for example, by addition of soluble salts, or by addition of mixtures of acids and bases, or by a combination thereof. It is a necessary aspect of the invention that both anions and cations of the ionic strength modifier system be included in the composition.

Suitable cations for use include, for example, alkali metals, such as lithium, sodium, and potassium, and alkaline-earth metals, such as magnesium, calcium, and strontium. Preferred of the divalent cations is magnesium. Preferred monovalent metal ions are lithium, sodium, and potassium, particularly sodium and potassium. Suitable means of addition to the compositions hereof include, for example, addition as bases, e.g., hydroxides, sodium hydroxide and potassium hydroxide, and such as salts that are soluble in the liquid carrier, e.g. salts of monomeric anions such as those described below.

Other suitable cations include organic ions, such as quaternary ammonium ions and cationic amines, such as ammonium mono-, di-, and tri-ethanolamines, triethylamine, morpholine, aminomethylpropanol (AMP), aminoethylpropanediol, etc. Ammonium and the amines are preferably provided in the forms of salts, such as hydrochloride salts.

Monomeric anions that can be used include halogen ions, such as chloride, fluoride, bromide, and iodide, particularly chloride, sulfate, ethyl

sulfate, methyl sulfate, cyclohexyl sulfamate, thiosulfate, toluene sulfonate, xylene sulfonate, citrate, nitrate, bicarbonate, adipate, succinate, saccharinate, benzoate, lactate, borate, isethionate, tartrate, and other monomeric anions that can exist in dissociated form in the hair styling composition. The anions can be added to the compositions hereof, for example, in the form of acids or salts which are at least partially soluble in the liquid vehicle, e.g., sodium or potassium salts of acetate, citrate, nitrate, chloride, sulfate, etc. Preferably, such salts are entirely soluble in the vehicle.

The use of ionic strength modifiers are especially useful in reduced volatile organic solvent compositions, most especially those utilizing silicone macromer-containing polymers.

Hair Styling Compositions

The present invention encompasses a wide variety of hair styling compositions, including hair spray compositions, mousses, and hair setting tonics. In general, the compositions will be flowable, low viscosity compositions that, preferably, are suitable for spray application. Higher viscosity compositions are also contemplated, however.

Hair spray compositions and mousses of the present invention can be dispensed from containers which are aerosol dispensers or pump spray dispensers. Such dispensers, i.e., containers, are well known to those skilled in the art and are commercially available from a variety of manufacturers, including American National Can Corp. and Continental Can Corp.

When the hair spray compositions are to be dispensed from a pressurized aerosol container, a propellant which consists of one or more of the conventionally-known aerosol propellants may be used to propel the compositions. A suitable propellant for use can be generally any liquifiable gas conventionally used for aerosol containers.

Suitable propellants for use are volatile hydrocarbon propellants which can include liquified lower hydrocarbons of 3 to 4 carbon atoms such as propane, butane and isobutane. Other suitable propellants are hydrofluorocarbons such as 1,2-difluoroethane (Hydrofluorocarbon 152A) supplied as Dymel 152A by DuPont. Other examples of propellants are dimethylether, nitrogen, carbon dioxide, nitrous oxide and atmospheric gas.

The hydrocarbons, particularly isobutane, used singly or admixed with other hydrocarbons are preferred.

The aerosol propellant may be mixed with the present compositions and the amount of propellant to be mixed is governed by normal factors well known in the aerosol art. Generally, for liquifiable propellants, the level of propellant is from about 10% to about 60% by weight of the total composition, preferably from about 15% to about 50% by weight of the total composition.

Alternatively, pressurized aerosol dispensers can be used where the propellant is separated from contact with the hair spray composition such as a two compartment can of the type sold under the tradename SEPRO from American National Can Corp.

Other suitable aerosol dispensers are those characterized by the propellant being compressed air which can be filled into the dispenser by means of a pump or equivalent device prior to use. Such dispensers are described in U.S. Patents 4,077,441, March 7, 1978, Olofsson and 4,850,577, July 25, 1989, TerStege, both incorporated by reference herein, and in U.S. Serial No. 07/839,648, Gosselin et al., filed February 21, 1992, also incorporated by reference herein. Compressed air aerosol containers suitable for use are also currently marketed by The Procter & Gamble Company under their tradename VIDAL SASSOON AIRSPRAY® hair sprays.

Conventional non-aerosol pump spray dispensers, i.e., atomizers, can also be used.

Other hair styling compositions include tonics and lotions, which are typically dispensed in a conventional bottle or tube, and applied directly to the hair or first dispensed to the hand and then to the hair.

The hair styling formulations of the present invention can optionally contain conventional hair care composition adjuvants. Generally, adjuvants collectively can comprise from about 0.05% to about 5% by weight and preferably from about 0.1% to about 3%, by weight. Such conventional optional adjuvants are well known to those skilled in the art and include in addition to those discussed above, emollients; lubricants and penetrants such as various lanolin compounds; protein hydrolysates and other protein derivatives; ethylene adducts and polyoxyethylene cholesterol; dyes, tints, bleaches, reducing agents and other colorants; pH adjusting agents sunscreens; preservatives;

thickening agents (e.g. polymeric thickeners, such as xanthan gum); and perfume.

METHOD OF MAKING

The hair styling compositions of the present invention can be made using conventional formulation and mixing techniques. Preferably, a premix of the silicone grafted polymer and the ethanol is made first. If ethanol is not to be used in the composition, a premix of the polymer with C₃ alkanol or water is prepared. The other ingredients can then be added with mixing to provide a homogeneous mixture. If the polymer is neutralized, the neutralizer is preferably added to the premix prior to addition of other ingredients.

METHOD OF USE

The compositions of the present invention are used in conventional ways to provide the hair styling/holding benefits of the present invention. Such method generally involves application of an effective amount of the product to dry, slightly damp, or wet hair before and/or after the hair is arranged to a desired style. The composition is then dried or allowed to dry. By "effective amount" is meant an amount sufficient to provide the hair hold and style benefits desired considering the length and texture of the hair. In general, from about 0.5g to about 30g of product will be applied to the hair, depending upon the particular product formulation, dispenser type, length of hair, and type of hair style.

The following Experimentals and Examples further illustrate embodiments within the scope of the present invention. They are given solely for the purposes of illustration and are not to be construed as limitations of the present invention as many variations of the invention are possible without departing from its spirit and scope.

EXPERIMENTALS

The following synthesis exemplify silicone grafted polymers useful in the present compositions.

Experimental 1: Batch synthesis

Place 20 parts acrylic acid, 60 parts t-butyl acrylate, and 20 parts polysiloxane (10,000 MW) -containing monomer in a flask. Add sufficient ethyl acetate or acetone as the reaction solvent to produce a final monomer concentration of 20%. Purge the vessel with an inert atmosphere, preferably nitrogen or argon. Add initiator, (2,2'-azobis-(2,4-dimethylvaleronitrile)) to a level appropriate for the desired molecular weight. Typically this is in the range of 0.5% to 1.0% by weight relative to

the amount of monomer. Purge the vessel with an inert atmosphere, preferably nitrogen or argon. Heat to 60°C and maintain this temperature for 48 hours while agitating. Terminate the reaction by cooling to room temperature. The polymer is purified by drying off the reaction solvent in an oven, or if acetone is used as the solvent precipitating the polymer, by adding water and then drying the precipitate.

Experimental 2: Semi-continuous synthesis

Place 20 parts acrylic acid, 60 parts t-butyl acrylate, and 30 parts polysiloxane (10,000 MW) -containing monomer in a flask. Add 300 parts ethyl acetate or acetone as the reaction solvent to produce a final monomer concentration of 20%. Purge the vessel with an inert atmosphere, e.g. nitrogen or argon. Add initiator, (2,2'-azobis-(2,4-dimethylvaleronitrile)) as in Experimental 1. Heat to 60°C and maintain this temperature. After polymerization of these monomers has proceeded about 15 minutes to about 1 hour, e.g. about 30 minutes, add a second monomer charge of 20 parts acrylic acid and 60 parts t-butyl acrylate, to give a final total monomer charge of approximately 40% by weight. Maintain at temperature for 48 hours. Terminate the reaction and purify the polymer as in Experimental 1.

EXAMPLES

Examples 1-6

The following examples represent nonaerosol hairspray compositions of the present invention.

Component (wt. %)	Example No					
	1	2	3	4	5	6
Silicone Grafted Polymer ¹	4.00	4.00	4.50	4.50	4.50	4.50
Isododecane ²	3.00	3.00	3.00	3.00	5.00	5.00
Acetyl triethyl citrate ³	0.20	--	0.22	--	--	--
Diisopropyl butyl adipate	--	--	--	0.22	0.32	--
Potassium hydroxide	0.40	0.40	0.45	0.45	0.44	0.44
Perfume	0.10	0.10	0.20	0.20	0.20	0.20
Water	16.00	16.10	7.00	7.00	15.54	15.86
Ethanol ⁴	75.30	75.50	84.62	84.63	74.00	74.00

¹ 60% t-butyl acrylate/20% acrylic acid/20% silicone macromer (weight average molecular weight of silicone macromer of about 10,000), having a weight average molecular weight of about 150,000.

² PERMETHYL 99A, from Presperse, Inc., South Plainfield, NJ, USA.

³ CITROFLEX A-2, from Morflex, Inc., Greensboro, NC, USA.

⁴ SDA 40 (100% ethanol).

5

Examples 7-10

The following examples represent aerosol hairspray compositions of the present invention.

Component (wt.%)	Example No.			
	<u>7</u>	<u>8</u>	<u>9</u>	<u>10</u>
Silicone Grafted Polymer ¹	3.50	3.50	3.50	3.50
Isododecane ²	3.00	3.00	3.00	3.00
Acetyl triethyl citrate ³	0.18	0.18	—	—
Diisopropyl butyl adipate	—	—	—	0.18
Potassium hydroxide	0.33	0.33	0.33	0.33
Perfume	0.10	0.10	0.10	0.10
Water	5.00	20.98	5.00	5.00
Ethanol ⁴	64.89	64.89	65.07	64.89
Propellant-Isobutane	7.02	7.02	7.02	7.02
Propellant-Hydrofluorocarbon 152a	15.98	—	15.98	15.98

¹ 60% t-butyl acrylate/20% acrylic acid/20% silicone macromer (weight average molecular weight of silicone macromer of about 10,000), having a weight average molecular weight of about 150,000.

² PERMETHYL 99A, from Presperse, Inc., South Plainfield, NJ, USA.

³ CITROFLEX A-2, from Morflex, Inc., Greensboro, NC, USA.

⁴ SDA 40 (100% ethanol).

In Examples 1-10, the compositions are prepared as described above, by first preparing a polymer premix with the ethanol, neutralizing the polymer with the potassium hydroxide (added as a 45% aqueous solution), then adding sequentially (as applicable) with mixing, water, isododecane, plasticizer, and perfume. Propellants for aerosol compositions are charged to conventional aerosol containers after the remainder of the prepared composition has been added.

EXAMPLE 11

A hair spray composition, of the present invention, which is suitable for use in pump spray dispensers, is prepared as follows:

	<u>Ingredient</u>	<u>Weight %</u>
5	Ethanol, 200 proof	75.92%
	Isopropanol	10.00%
	Silicone Grafter Polymer ¹	3.00%
	KOH (45%) ²	0.88%
	DRO Water ³	7.00%
10	Isododecane	3.00%
	Fluorad FC-109R (25%) ⁴	0.20%

1 60% t-butyl acrylate/20% acrylic acid/20% silicone macromer weight average mw=10,000, having a weight average molecular weight of about 690,000.

15 2 Potassium hydroxide solution, containing 45% potassium hydroxide and 55% water and minors, supplied by Fisher Scientific.

3 Double reverse osmosis water

4 Fluorad FC-109R supplied by 3M containing 25% potassium fluoroalkyl carboxylates (an anionic fluorosurfactant), 12% propanol, 2% ethanol and 61% water and minors.

20 The hair spray formulation of Example II is prepared by preparing a premix of the resin in isopropanol. The isopropanol premix is added to the ethanol and then neutralized with the potassium hydroxide solution. Then, a premix of the fluorosurfactants and water is prepared and added to the neutralized premix. Isododecane is then added. Other adjuvants, such as fragrances, may then be added. A magnetic or air driven stirrer is used to mix the ingredients until the resin is dissolved.

EXAMPLE 12

30 A hair spray composition, of the present invention, which is suitable for use in pump spray dispensers, is prepared as follows:

	<u>Ingredient</u>	<u>Weight %</u>
	Ethanol, 200 proof	84.45%
	Silicone Grafter Polymer ¹	3.00%
	KOH (45%)	0.88%
35	DRO Water	7.00%
	Isododecane	5.00%
	Zonyl FSK ^R (47%) ²	0.11%

1 60% t-butyl acrylate/20% acrylic acid/20% silicone macromer
weight average mw=10,000, having a weight average molecular weight
of about 690,000.

2 Zonyl FSK^R containing 47% fluorosurfactants conforming to the
5 formula $R_f\text{CH}_2\text{CH}(\text{OCOCH}_3)\text{CH}_2\text{N}^+(\text{CH}_3)_2\text{CH}_2\text{CO}_2$ wherein
 $R_f=\text{F}(\text{CF}_2\text{CF}_2)_{3-8}$ and 53% Acetic Acid and minors, having a zwitterionic
character, supplied by DuPont.

This composition is prepared as in Example 11.

EXAMPLE 13

10 A hair spray composition, of the present invention, which is
suitable for use in pump spray dispensers, is prepared as follows:

	<u>Ingredient</u>	<u>Weight %</u>
	Ethanol, 200 proof	76.10%
	Isopropanol	10.40%
15	Silicone Grafter Polymer ¹	2.60%
	KOH (45%)	0.75%
	DRO Water	7.00%
	Isopar TM H (Exxon Chemical) ²	3.00%
	Fluorad FC-120 ^R (25%) ³	0.10%
20	Zonyl FSK (47%)	0.05%

1 60% t-butyl acrylate /20% acrylic acid/20% silicone macromer
weight average mw=10,000, having a weight average molecular weight
of about 800,000.

2 IsoparTM H is a C₁₁₋₁₂ Isoparaffin

25 3 Fluorad FC-120^R supplied by 3M, having an anionic character
and containing 25% mixed ammonium perfluoroalkyl sulfonates, 37.5%
ethanol, and 37.5% water and minors.

This composition is prepared as in Example 11, substituting Isopar
H for isododecane during processing.

30 EXAMPLE 14

A hair spray composition, of the present invention, which is
suitable for use in pump spray dispensers, is prepared as follows:

	<u>Ingredient</u>	<u>Weight %</u>
35	Ethanol, 200 proof	75.86%
	Isopropanol	10.40%
	Silicone Grafted Polymer ¹	2.60%

30

	KOH (45%)	0.69%
	DRO Water	7.00%
	Isopar TM L (Exxon Chemical) ²	3.00%
	Fluorad FC-120 ^R (25%)	0.40%
5	Zonyl FSK ^R (47%)	0.05%
1	60% t-butyl acrylate /20% acrylic acid/20% silicone macromer weight average mw=10,000, having a weight average molecular weight of about 1,700,000.	
2	Isopar TM L is a C ₁₁₋₁₃ Isoparaffin	
10	This composition is prepared as in Example 13.	

EXAMPLE 15

A hair spray composition, of the present invention, which is suitable for use in pump spray dispensers, is prepared as follows:

	<u>Ingredient</u>	<u>Weight %</u>
15	Ethanol, 200 proof	86.55%
	Silicone Grafted Polymer ¹	2.60%
	KOH (45%)	0.75%
	DRO Water	7.00%
	Isopar TM M(Exxon Chemical) ²	3.00%
20	Fluorad FC-135 ^R (50%) ³	0.10%
1	60% t-butyl acrylate/20% acrylic acid/20% silicone macromer weight average mw=20,000, having a weight average molecular weight of about 800,000.	
2	Isopar TM M is a C ₁₃₋₁₄ Isoparaffin	
25	3 Fluorad FC-135 ^R supplied by 3M, having anionic character and containing 25% mixed ammonium perfluoroalkyl sulfonates, 37.5% ethanol and 37.5% water and minors.	

This composition is prepared as in Example 13.

What is claimed is:

1. A Hair styling composition characterized in that it comprises:

- (a) from 0.1% to 15%, by weight, of a silicone grafted adhesive polymer, said polymer being characterized by an organic polymeric backbone having silicone macromers grafted to said backbone;
- (b) from 0.5% to 15%, by weight, of a hydrocarbon solvent selected from the group consisting of C₁₀-C₁₄ branched chain hydrocarbons, and mixtures thereof having a boiling point of from 105°C to 260°C;
- (c) a polar solvent phase comprising from 80% to 98.9%, by weight of the composition, of a polar solvent selected from the group consisting of water and C₂-C₃ monohydric alcohols, and mixtures thereof, wherein said composition contains no more than 15%, by weight, of C₃ monohydric alcohol;

wherein said organic polymer backbone is soluble in said polar solvent phase, and said silicone macromers of said hair setting polymer are soluble in said hydrocarbon solvent and insoluble in said polar solvent.

2. A hair styling composition as in Claim 1, wherein said composition comprises:

- (a) from 0.5% to 8%, by weight, of said silicone grafted polymer;
- (b) from 1% to 10%, by weight, of said hydrocarbon solvent;
- (c) from 85% to 98%, by weight, of said polar solvent, wherein said composition contains no more than 12%, by weight, of C₃ monohydric alcohol.

3. A hair styling composition as in Claim 1, wherein said composition comprises:

- (a) from 1% to 8%, by weight, of said silicone grafted polymer;
- (b) from 2% to 8%, by weight, of said hydrocarbon solvent;
- (c) from 80% to 98.9%, by weight, of said polar solvent, wherein said composition contains no more than 12%, by weight, of C₃ monohydric alcohol and said composition contains at least 10%, by weight, of water and no more than 80%, by weight, of volatile organic compounds.

4. A hair styling composition as in Claim 1, 2, or 3, wherein said silicone grafted polymer comprises from 50% to 99%, preferably from 75% to 95%, by weight, of non-silicone macromer-containing monomer units and from 1% to 50%,

preferably from 29% to 25%, by weight of silicone macromer-containing monomer units.

5. A hair styling composition as in Claim 4, wherein said silicone grafted polymer comprises from 1% to 99%, preferably from 15% to 40%, by weight, of hydrophilic monomer units and from 0% to 99%, preferably from 15% to 80%, by weight, of hydrophobic monomer units.

6. A hair styling composition as in Claim 5, wherein said hydrophilic monomer units are selected from the group consisting of acrylic acid, N,N-dimethyl acrylamide, dimethylaminoethyl methacrylate, quaternized dimethyl aminoethyl methacrylate, vinyl pyrrolidone, salts of acids and amines thereof, and mixtures thereof.

7. A hair styling composition as in Claim 6, wherein said hydrophobic monomer units are selected from the group consisting of n-butyl methacrylate, isobutyl methacrylate, t-butyl acrylate, t-butyl methacrylate, 2-ethylhexyl methacrylate, methyl methacrylate, and mixtures thereof, preferably selected from the group consisting of t-butyl acrylate, t-butyl methacrylate, and mixtures thereof.

8. A hair styling composition as in Claim 1, 2, 3, 4, 5, 6, or 7, wherein said hydrocarbon solvent is selected from the group consisting of saturated C₁₁-C₁₃ branched chain hydrocarbons, preferably isododecane.

9. A hair styling composition as in Claim 1, 2, 3, 4, 5, 6, 7, or 8, wherein said composition further comprises a plasticizer selected from the group consisting of acetyl tri-C₂-C₈alkyl citrates, and mixtures thereof, preferably acetyl triethyl citrate.

10. A hair spray composition comprising a composition as in Claim 1, 2, 3, 4, 5, 6, 7, 8, Or 9, disposed within a hair spray dispenser.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 94/08031

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A61K7/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP,A,0 408 311 (MITSUBISHI) 16 January 1991 cited in the application ---	1-10
Y	WO,A,93 03704 (PROCTER & GAMBLE) 4 March 1993 see the whole document -----	1-10

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

13 October 1994

Date of mailing of the international search report

26. 10. 94

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+ 31-70) 340-3016

Authorized officer

Klaver, T

INTERNATIONAL SEARCH REPORT

information on patent family members

Inter. Application No

PCT/US 94/08031

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0408311	16-01-91	JP-A- 3128909 US-A- 5166276	31-05-91 24-11-92
WO-A-9303704	04-03-93	AU-A- 2502892 CA-A- 2115154 EP-A- 0600008 FI-A- 940771	16-03-93 04-03-93 08-06-94 18-02-94

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : A61K 7/11	A1	(11) International Publication Number: WO 95/32703 (43) International Publication Date: 7 December 1995 (07.12.95)
(21) International Application Number: PCT/US95/04756 (22) International Filing Date: 18 April 1995 (18.04.95) (30) Priority Data: 9410783.6 28 May 1994 (28.05.94) GB (71) Applicant (for all designated States except US): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): COOPER, Elizabeth, Claire [GB/GB]; 27 Heath Gardens, Twickenham, Middlesex TW1 4LY (GB). WELCH, Rosemary, Janue [GB/GB]; 15 Thorncroft, Englefield Green, Surrey TW20 0SB (GB). (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).		(81) Designated States: AU, BR, CA, CN, JP, KR, MX, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: HAIR COSMETIC COMPOSITIONS (57) Abstract A liquid hair cosmetic composition comprising: (a) from about 0.1 % by weight to about 10 % by weight (acid basis) of a silicone-containing polycarboxylic acid copolymer having a vinyl polymeric backbone, and having grafted to the backbone a silicone-containing macromer having a weight average molecular weight of from about 1,000 to about 50,000; (b) a neutralising system consisting essentially of sodium hydroxide present at a level sufficient to neutralise at least about 25 % of the acid groups on the silicone-containing copolymer; (c) from 0 % to about 1.0 % by weight of water; and (d) the balance comprising a carrier suitable for application to hair. The liquid hair cosmetic products have improved clarity and storage stability and demonstrate excellent hair styling benefits in addition to hair feel attributes and ease of removal and brush out.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

HAIR COSMETIC COMPOSITIONS

Technical Field

The present invention relates to hair cosmetic compositions. More particularly, this invention relates to liquid hair cosmetic compositions containing silicone-grafted hair styling polymers having improved long term product stability, hair feel attributes and ease of removal and brush out as well as excellent style retention properties.

Background Of The Invention

The desire to have the hair retain a particular shape is widely held. A common methodology for accomplishing this is applying hair styling, or "setting" compositions to the hair, typically to damp or dry hair. These compositions provide temporary setting benefits, and should be removable by water and/or by shampooing. The materials used in the compositions to provide the setting benefits are generally applied in the form of mousses, gels, lotions or sprays.

High levels of style retention, or hold, are typically expected from hair styling compositions applied as a spray. Style retention is typically achieved by the use of resins, such as AMPHOMER, supplied by National Starch, and GANTREZ SP 225, supplied by GAF. As used in commercially sold hairspray products, these resins generally have a weight average molecular weight of from about 40,000 to about 150,000.

When such resins are incorporated into pump and aerosol hairsprays, they can provide suitable style retention attributes. However, such resins are found to be deficient in the area of hair feel and can give a stiff hair feel.

Recently, it has been found that certain neutralisable polymers having silicone macromer portions can provide good style retention benefits to the hair while also providing improved hair feel. In other words, such silicone macromer-containing polymers can impart a tactile sense of softness and conditioning to the hair relative to conventional, non-silicone-containing resins without the tacky hair feel traditionally associated with non-silicone hair fixative polymers. Silicone macromer-containing hair styling polymers and formulations containing them are disclosed, for example, in EP-A-0,408,311 A2 issued January 11th 1991, Hayama, et al., US-A-5,061,481, issued October 29th 1991, Suzuki et al., US-A-5,106,609, Bolich et al., issued April 21st 1992, US-A-5,100,658, Bolich et al., issued March 31st 1992, US-A-5,100,657, Ansher-Jackson, et al., issued March 31st 1992 and US-A-5,104,646, Bolich et al., issued April 14th 1992.

It is well known that at least partial neutralisation of the silicone macromer-containing hair styling polymer is necessary to maximise its utility in hair styling compositions. Typically, silicone grafted co-polymers neutralised with potassium hydroxide exhibit good solubility in hairspray compositions containing 15% water. However, potassium hydroxide neutralised systems are less soluble in compositions which contain lower levels of water and lead to hazy, colloidal systems. Moreover, silicone grafted co-polymers which are neutralised with organic neutralisers are found to lead to a somewhat tacky hair feel and are not easily removed from the hair by washing or brush-out.

Thus a need exists for hair styling compositions which have a clear appearance, deliver effective style retention, impart a hair conditioning effect, have a non-sticky hair feel, are easily brushed out and at the same time have stable product and viscosity characteristics and remain fully stable under long term and stressed temperature storage.

Summary of the Invention

According to one aspect of the invention, there is provided a liquid hair cosmetic composition comprising:-

- (a) from about 0.1 % by weight to about 10% by weight (acid basis) of a silicone-containing polycarboxylic acid copolymer having a vinyl polymeric backbone, and having grafted to the backbone a silicone-containing macromer having a weight average molecular weight of from about 1,000 to about 50,000;
- (b) a neutralising system consisting essentially of sodium hydroxide present at a level sufficient to neutralise at least about 25 % of the acid groups on the silicone-containing copolymer;
- (c) from 0% to about 1.0% by weight of water; and
- (d) the balance comprising a carrier suitable for application to hair.

The essential, as well as the optional, components of the present invention are described below. All levels and ratios are on a weight basis unless otherwise specified.

The compositions of the present invention contain from about 0.1 % to about 10.0%, preferably from about 0.5% to about 8.0% and especially from about 1 % to about 6% of specifically defined silicone-containing copolymers. It is these polymers which provide the unique hair conditioning and hair setting characteristics of the present invention. The polymers preferably have a weight average molecular weight of from about 10,000 to about 1,000,000, preferably from about 30,000 to about 300,000, most preferably from about 90,000 to about 300,000 and, preferably, have a Tg of at least about -20°C. As used herein, the abbreviation "Tg" refers to the glass transition temperature of the non-silicone backbone, and the abbreviation "Tm" refers to the crystalline melting point of the non-silicone backbone, if such a transition exists for a given polymer.

The molecular weights and molecular weight distributions of the polymers utilised in the compositions according to the present invention are determined by Size Exclusion Chromatography (SEC). In practise, polymers comprise a distribution of molecular weight species that gives rise to their unique properties. Separation of the molecules is accomplished by Size Exclusion Chromatography (SEC) using a crosslinked polystyrene -divinylbenzene column (MW range = $100 - 10^7$) with a differential refractive index detector and a differential viscometer. A universal calibration curve is prepared from monodispersed polystyrene standards of known molecular weight (MW) and molecular weight distribution (MWD). MW and MWD of the given polymer are determined based on concentration and viscosity responses relative to the calibration.

Preferred polymers comprise a vinyl polymeric backbone, preferably having a T_g above about -20°C and, grafted to the backbone, a silicone-containing macromer having a weight average molecular weight of from about 1,000 to about 50,000, preferably from about 5,000 to about 40,000, most preferably from about 10,000 to about 20,000. The polymer is such that when it is formulated into the finished hair care composition, when dried, the polymer phase separates into a discontinuous phase which includes the silicone containing macromer and a continuous phase which includes the backbone. It is believed that this phase separation property provides a specific orientation of the polymer on hair which results in the desired hair conditioning and setting benefits.

In its broadest aspect, the copolymers utilized in the present application comprise a silicone-containing monomer (hereafter identified as C) together with a hydrophilic carboxylate-containing monomer (B) and optionally a lipophilic monomer (A).

Examples of useful copolymers and their preparation are described in detail in US-A-4,693,935, Mazurek, issued September 15th 1987, and US-A-4,728,571, Clemens et al., issued March 1st 1988. These copolymers comprise monomers A, B and C as defined above. In preferred embodiments, A comprises at least one free radically polymerizable vinyl monomer or monomers and B comprises at least one

reinforcing monomer copolymerizable with A and selected from the group consisting of carboxylate-containing monomers and macromers having a T_g or a T_m above about -20°C . B can be up to about 98%, preferably up to about 80%, more preferably up to about 30%, of the total monomers in the copolymer. Monomer C comprises from about 0.1% to about 50.0% of the total monomers in the copolymer.

Representative examples of A (hydrophobic) monomers are the acrylic or methacrylic acid esters of C_1 - C_{18} alcohols, such as methanol, ethanol, methoxy ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 1-methyl-1-butanol, 3-methyl-1-butanol, 1-methyl-1-pentanol, 2-methyl-1-pentanol, 3-methyl-1-pentanol, t-butanol (2-methyl-1-propanol), cyclohexanol, neodecanol, 2-ethyl-1-butanol, 3-heptanol, benzyl alcohol, 2-octanol, 6-methyl-1-heptanol, 2-ethyl-1-hexanol, 3,5-dimethyl-1-hexanol, 3,5,5-trimethyl-1-hexanol, 1-decanol, 1-dodecanol, 1-hexadecanol, 1-octadecanol, and the like, the alcohols having from about 1-18 carbon atoms with the average number of carbon atoms being from about 4-12; styrene; polystyrene macromer; vinyl acetate; vinyl chloride; vinylidene chloride; vinyl propionate; alpha-methylstyrene; t-butylstyrene; butadiene; cyclohexadiene; ethylene; propylene; vinyl toluene; and mixtures thereof. Preferred A monomers include n-butyl methacrylate, isobutyl methacrylate, 2-ethylhexyl methacrylate, methyl methacrylate, t-butylacrylate, t-butylmethacrylate, and mixtures thereof.

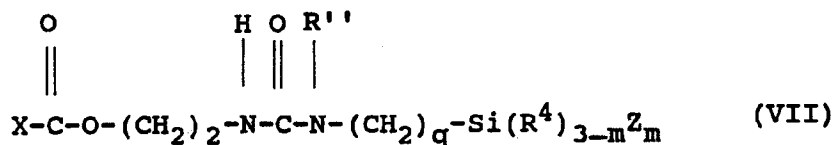
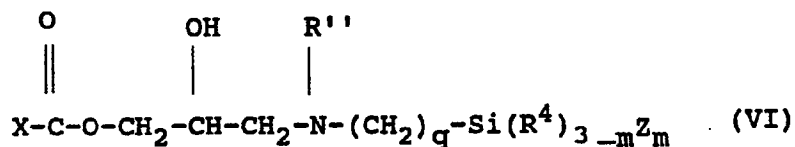
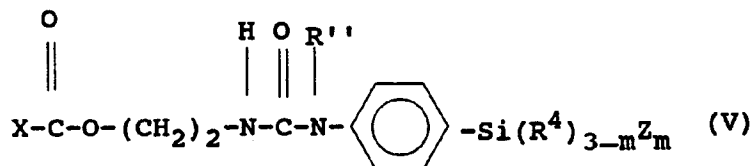
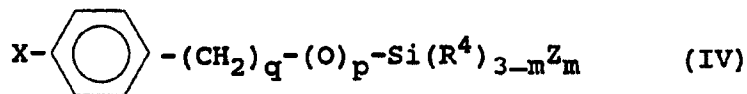
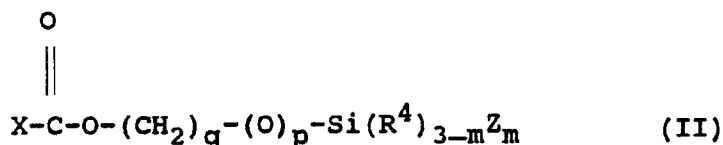
Representative examples of B (hydrophilic) neutralisable monomers containing a carboxyl moiety include acrylic acid, methacrylic acid, maleic acid, maleic anhydride, half esters of maleic anhydride, crotonic acid, and itaconic acid. Preferred B monomers include acrylic acid and methacrylic acid and mixtures thereof.

The C monomer preferably has the general formula (I):



wherein X is a vinyl group copolymerizable with the A and B monomers; Y is a divalent linking group; R is hydrogen, C_1 - C_4 alkyl, aryl, alkyl

amino, tri(C₁-C₄ alkyl)siloxy or C₁-C₄ alkoxy; Z is a monovalent siloxane polymeric moiety; n is 0 or 1; and m is an integer from 1 to 3. C has a number average molecular weight of, at least 500, preferably from 1,000 to 50,000. Preferably, the C monomer is selected from one or more monomers having the general formulae (II to VII):



In these structures, m is 1, 2 or 3 (preferably m = 1); p is 0 or 1; R'' is alkyl or hydrogen; q is an integer from 2 to 6; X is



R^1 is hydrogen or $-\text{COOH}$ (preferably R^1 is hydrogen); R^2 is hydrogen, methyl or $-\text{CH}_2\text{COOH}$ (preferably R^2 is methyl); Z is



R^4 is alkyl, alkoxy, alkylamino, aryl, or hydroxyl (preferably R^4 is alkyl); and r is an integer from 5 to 700, preferably from 50 to 500, more preferably from 150 to 300. Of the above, formula II is preferred, particularly when $p = 0$ and $q = 3$.

The polymers utilized herein generally comprise from 0% to about 98% (preferably from about 5% to about 92%, more preferably from about 50% to about 90%) of monomer A, from about 1% to about 98% (preferably from about 7.5% to about 80%) of monomer B, and from about 0.1% to about 50% (preferably from about 0.5% to about 40%, most preferably from about 2% to about 25%) of monomer C. The combination of the A and B monomers preferably comprises from about 50.0% to about 99.9% (more preferably about 60% to about 99.5%, most preferably from about 75% to about 98%) of the polymer.

Preferred silicone-containing copolymers for use herein are selected from:

acrylic acid/n-butylmethacrylate/polydimethylsiloxane (PDMS)
macromer-20,000 molecular weight (mw) (10/70/20 w/w/w)

acrylic acid/isobutyl methacrylate/PDMS macromer - 20,000 mw
(20/60/20 w/w/w)

acrylic acid/PDMS macromer - 20,000 mw (80/20 w/w)

t-butylacrylate(tBA)/acrylic acid(AA)/PDMS macromer - 10,000 mw
(60/20/20)

acrylic acid/isobutyl methacrylate/PDMS macromer - 20,000 mw
(10/70/20);

acrylic acid/methyl methacrylate/PDMS macromer - 20,000 mw
(40/40/20);

acrylic acid/isopropyl methacrylate/PDMS macromer - 20,000 mw
(25/65/15);

acrylic acid/methoxyethyl methacrylate/PDMS macromer 20,000 mw
(60/25/15);

acrylic acid/PDMS macromer - 20,000 mw (80/20);
and mixtures thereof.

The silicone-containing copolymers described above can be synthesized by free radical polymerization of silicone- or polysiloxane-containing monomers with non-silicone- or non-polysiloxane-containing monomers. The general principles of free radical polymerization methods are well understood. See, for example, Odian, "Principles of Polymerization", 2nd edition, John Wiley & Sons, 1981, pp. 179 - 318.

In compositions according to the invention it can be desirable to purify the silicone containing copolymer by removing unreacted silicone-containing monomer and silicone macromer-grafted polymer with viscosities at 25°C of about 10,000,000 centistokes and less. This can be done, for example, by hexane extraction. After drying the resin from its reaction solvent, hexane extraction of the reaction product can be performed by adding an excess of hexane to the reaction product and heating to near the T_g of the non-silicone portion of the polymer. The mixture is held at this temperature with stirring for about 30 minutes and cooled to room temperature. The hexane is removed by vacuum suction. Two more hexane extraction cycles are preferably conducted in the same manner as

above. After the third cycle, residual hexane remaining with the product is removed by distillation and vacuum drying.

Low molecular weight polysiloxane-containing monomer and polymer is solubilized by supercritical carbon dioxide and transported away from the remaining polymer via a transfer line, which is maintained at identical temperature and pressure as the extraction vessel. The extracted materials are collected in an extraction vessel. Following extraction, the system is depressurised and dry, extracted polymer is recovered from the extraction vessel.

The hair styling polymers herein are utilised in at least partially neutralised form in order to aid shampoo removability of the liquid hair cosmetic compositions. The present development relates to the neutralisation of a hair fixative polymer (eg silicone grafted tBA/AA copolymer) with a neutralisation system consisting essentially of a specific inorganic base, namely sodium hydroxide, in anhydrous or essentially anhydrous aerosol and non-aerosol hairsprays and other hair cosmetic products. In particular the present development relates to improving the clarity, long term storage stability, hair feel attributes and ease of removal characteristics of hairspray and other hair cosmetic products containing no or very low levels of water, approximately 0 - 1%, preferably 0 - 0.7% water, by neutralisation of the hair fixative polymer with a neutralisation system comprising at least 80%, preferably at least 95% and more preferably at least 99% by weight of the neutralisation system of sodium hydroxide. While the neutralisation system can be used in excess of the polymer (for example up to 15% excess on an equivalent basis) so as to result effectively in 100% neutralisation of the polymer, nevertheless in preferred compositions, a total of from about 25% to about 95%, preferably from about 40% to about 90%, more preferably from about 55% to about 85%, and especially from about 65% to about 80% of the acidic monomers of the polymer are neutralised.

The amount in grams of inorganic base (Z) required to neutralise a polymer can be deduced from calculations which take into account the acid value of the polymer (A); amount of polymer (W); mol wt of the

base (B); mol wt of the acidic moiety (M) and the degree of neutralisation required (N).

$$Z(g) = W \times A/100 \times 1/M \times B \times N\%$$

In the following example the amount of NaOH required to neutralise 2.6g of acrylic acid co-polymer (with acid value of 20) to a level of 77% neutralisation is calculated.

$$Z(g) = 2.6 \times 20/100 \times 1/72 \times 40 \times 0.77$$

$$Z = 0.222 \text{ g}$$

Note the acid value can be experimentally determined by titrating a specific amount of the polymer with base or theoretically by considering the original acidic content of the co-polymer i.e. a polymer with 20% of acid monomer has an acid value of 20.

As described earlier herein, use of the herein defined neutralising system for at least partial neutralisation of the silicone grafted copolymer leads to anhydrous or essentially anhydrous liquid hair cosmetic compositions of improved clarity and long term storage stability. Product clarity can be measured using a visible range spectrophotometer. Using this equipment the percent transmittance of the sample at 450 nm is measured by calibration against a reference sample of Ethanol B100 as 100% transmittance. Typical transmittance values for opaque systems neutralised with potassium hydroxide neutraliser can be as low as from 1 to 5%. In contrast, the compositions of the invention typically display percent transmittance values greater than 80% when first made, preferred compositions herein displaying 80% transmittance values after storage for at least four weeks at 45 C.

The liquid hair cosmetic compositions of the present invention also include a carrier. This can comprise any of those conventionally used in resin hairspray formulations inclusive of solvents, propellants and other optional ingredients of liquid hair cosmetics. The carrier is generally present in the liquid hair cosmetic compositions at from about 70% to

about 99.8%, preferably from about 78% to about 99% by weight. More preferably, the carrier is present at from about 80% to about 98% by weight of the total composition.

Organic solvents suitable for use in the carrier of the present compositions include C₁-C₆ alkanols and ethers, carbitol, acetone and mixtures thereof. C₁-C₆ alkanols preferred for use in the present compositions are C₂-C₄ monohydric alcohols such as ethanol, isopropanol and mixtures thereof. Dimethoxymethane is also a highly preferred solvent.

The performance of the liquid hair cosmetic compositions according to the invention can be improved through the optional incorporation of a nonvolatile plasticizer into the composition. The plasticizer will generally be present in the compositions at up to a level of 25%, preferable from 1% to 20%, more preferably from 1% to 15%. As used herein, "nonvolatile" in regard to plasticizers means that the plasticizer exhibits essentially no vapour pressure at atmospheric pressure and 25°C. The polymer-liquid vehicle solution should not suffer from substantial plasticizer weight loss while the hair cosmetic carrier is evaporating, since this may excessively reduce plasticization of the polymer during use. The plasticizers for use herein should generally have boiling points of about 250°C or higher.

Plasticizers are well known in the art and are generally described in Kirk-Othmer Encyclopedia of Chemical Technology, second edition, Volume 15, pp. 720-789 (John Wiley & Sons, Inc. New York, 1968) under the topic heading "Plasticizers", and by J. Kern Sears and J. R. Darby in the text The Technology of Plasticizers (John Wiley & Sons, Inc., New York, 1982). See especially in the Appendix of Sears/Darby Table A.9 at pages 983-1063 where a wide variety of plasticizers are disclosed.

Plasticizers suitable for use in compositions of the present invention include both cyclic and acyclic nonvolatile materials. Suitable categories of nonvolatile plasticizers include adipates, phthalates, isophthalates, azelates, stearates, citrates, trimellitates, silicone copolyols, iso C₁₄-C₂₂ alcohols, methyl alkyl silicones, carbonates, sebacates, isobutyrate, oleates, phosphates, myristates, ricinoleates, pelargonates, valerates,

camphor, glycols, amine derivatives, selected short chain alcohols and castor oil.

Particularly preferred plasticizers for use herein include glycol and citrate based plasticizers such as propylene glycol, dipropylene glycol, acetyl tri-n-butyl citrate, triethylcitrate, tri-n-butyl and acetyl tri-2-ethoxyhexyl citrate (as supplied by Pfizer under the trade name Citroflex (RTM) and also glycerin, amino methyl propanol (AMP), diisobutyladipate (DIBA) and isopropanol.

The present compositions can be formulated as hairsprays in aerosol or non-aerosol forms. If an aerosol hairspray is desired, a propellant must be included in the composition. This agent is responsible for expelling the other materials from the container and forming the hairspray character.

The propellant gas can be any liquefiable gas conventionally used for aerosol containers. Preferably the density of the propellant or mixture thereof is less than 1 so that pure propellant is not emitted from the container. Examples of materials that are suitable for use as propellants are trichlorofluoromethane, dichlorodifluoromethane, dichlorotetrafluoroethane, monochlorodifluoromethane, trichlorotrifluoroethane, dimethylether e.g Dimel 152A (RTM) supplied by Du Pont, propane, n-butane, isobutane, used singly or admixed and propane butane e.g CAP 80 (RTM). Dimel 152A (RTM) and propane butane are preferred.

The amount of the propellant gas is governed by normal factors well known in the aerosol art. For hairsprays the level of propellant is generally from about 10% to about 40%, preferably from about 20% to about 30%, of the total composition. If a propellant such as dimethylether utilizes vapor pressure suppressant (e.g., trichloroethane or dichloromethane) the amount of suppressant is included as part of the propellant.

The hair spray compositions of the present invention can be made using conventional formulation and mixing techniques. Compositions of the

present invention can be made by adding the polymer to ethanol and mixing for several hours until dissolved. Plasticizer and neutralising ingredients are then added and the resulting solution is stirred. Any remaining ingredients such as water, ethanol and perfume can then be added.

Methods of making the hair cosmetic compositions of the present invention are described more specifically in the examples.

Alternatively, pressurised aerosol dispensers can be used where the propellant is separated from contact with the hairspray composition by use of specialised containers such as a two compartment can of the type sold under the tradename SEPRO from Americal National Can Corp.

Other suitable aerosol dispensers are those characterized by the propellant being compressed air which can be filled into the dispenser by means of a pump or equivalent device prior to use. Such dispensers are described in US-A-4,077,441, March 7th 1978, Olofsson and US-A-4,850,577, July 25th 1989, TerStege. Compressed air aerosol containers suitable for use are also currently marketed by The Procter & Gamble Company under their tradename VIDAL SASSOON AIRSPRAY (RTM) hairsprays.

Conventional non-aerosol pump spray dispensers, i.e., atomizers, can also be used.

The liquid hair cosmetic compositions of the present invention can also contain a variety of non-essential, optional components such as preservatives, surfactants, block polymers, thickeners and viscosity modifiers, electrolytes, fatty alcohols, pH adjusting agents, spreading agents, perfume oils, perfume solubilizing agents, sequestering agents; emollients; lubricants and penetrants such as various lanolin components; protein hydrolysates and other protein derivatives; ethylene adducts and polyoxyethylene cholesterol; sunscreens and volatile and non-volatile silicone fluids. Such conventional optional ingredients are well known to a person skilled in the art, e.g. surfactants such as anionics (e.g., sodium alkyl sulphates, nonionics (amine oxides) ; amphoterics (aliphatic secondary or tertiary amine derivatives) zwitterionics (aliphatic

quaternary ammonium; phosphonium or sulphonium derivatives) and fluorinated surfactants (e.g. Zonyl FSK) (RTM); thickeners and viscosity modifiers such as diethanolamides of long chain fatty acids; block polymers of ethylene oxide and propylene oxide such as Pluronic (RTM) F88 offered by BASF Wyandotte; fatty alcohols such as cetearyl alcohol; viscosity modifiers such as sodium chloride, sodium sulphate, and ethyl alcohol; electrolyte such as earth and alkaline-earth metal salts; quaternary ammonium ions and cationic amines and halogen ions; pH adjusting agents such as citric acid, succinic acid, sodium hydroxide and triethanolamine; spreading agents such as isododecane, perfume oils such as Florasynth (RTM) perfumes; perfume oil solubilizers such as polyethylene glycol fatty acid esters and sequestering agents such as ethylenediamine tetraacetic acid. Each of these optional materials can be present at a level of from about 0.05% to about 5%, preferably from about 0.1% to about 3% by weight of composition.

The liquid hair cosmetic compositions of the present invention are used in conventional ways to provide the hair styling/holding benefits of the present invention. Such method generally involves spraying an effective amount of the product to dry or damp hair before or after the hair is styled, or both. By "effective amount" is meant an amount sufficient to provide the hair volume and style benefits desired considering the length and texture of the hair.

The invention is illustrated by the following non-limiting examples.

In the examples, all concentrations are on a 100% active basis, unless otherwise stated and the abbreviations have the following designation:

Hair Styling Polymer - 60% t-butyl acrylate/20% acrylic acid/20% silicone PDMS. Weight average molecular weight (measured by SEC) of 150,000.

NaOH - Sodium hydroxide solution, containing 45% sodium hydroxide and 55% water.

Solvent - Ethanol

Examples I-VI

The following are liquid hair cosmetic compositions in the form of hairspray compositions suitable for pump spray dispensers and which are representative of the present invention:

	I	II	III	IV	V	VI
Hair Styling Polymer	3.0	2.0	4.0	6.0	2.0	5.0
% poly NaOH neutralised	82	70	75	80	85	75
Balance	-----to 100 percent with ethanol-----					

The balance contains ethanol and optional ingredients such as plasticizer (preferably DIBA), perfume and surfactants.

The hairspray formulations are prepared by adding the polymer directly to the ethanol. A magnetic or air driven stirrer is used to mix the ingredients until the polymer is dissolved, typically about 1 to 2 hours. The neutralizing agent is then added and mixed into the premix. Then, the optional ingredients, as may be applicable, are mixed into the composition.

The above compositions provide effective style retention, deliver a hair conditioning effect and have excellent long term clarity and a non-tacky hair feel.

Examples VII-XII

The following are liquid hair cosmetic compositions in the form of hairspray concentrate compositions suitable for aerosol dispensers and which are representative of the present invention:

VII VIII IX X XI XII

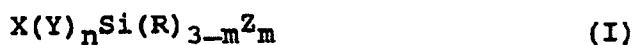
Hair Styling Polymer	4.0	2.0	5.0	6.0	3.0	7.0
% poly NaOH neutralised	70	78	85	78	80	75
Balance	----- to 100 percent with solvent -----					

As in examples I to VI the balance is ethanol and optional ingredients such as plasticizer (preferably DIBA), perfume and surfactants. The above compositions are prepared as in Examples I-VI. The concentrates are packaged in conventional aerosol spray cans and are charged with a conventional liquifiable propellant such as CAP 80 (RTM) at a propellant:concentrate weight ratio of 23:77.

The above compositions have excellent clarity and stability characteristics and when applied to the hair, provide good hair styling and conditioning benefits as well as a non-tacky hair feel and improved ease of removal.

WHAT IS CLAIMED IS:

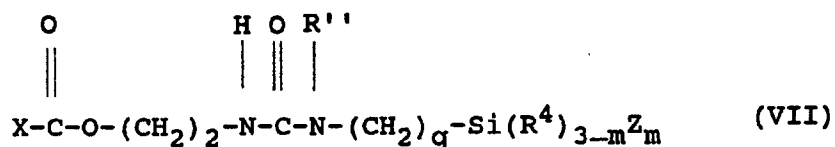
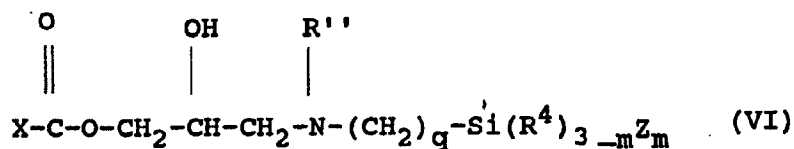
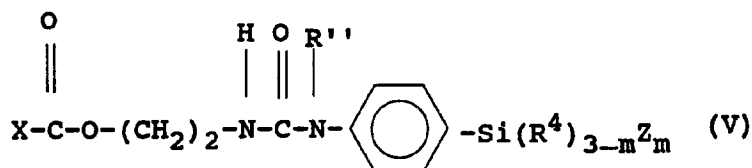
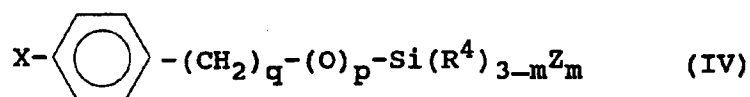
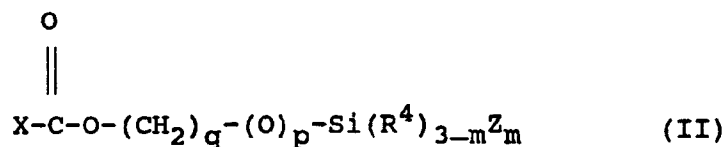
1. A liquid hair cosmetic composition comprising:-
 - (a) from about 0.1 % by weight to about 10% by weight (acid basis) of a silicone-containing polycarboxylic acid copolymer having a vinyl polymeric backbone, and having grafted to the backbone a silicone-containing macromer having a weight average molecular weight of from about 1,000 to about 50,000;
 - (b) a neutralising system consisting essentially of sodium hydroxide present at a level sufficient to neutralise at least about 25% of the acid groups on the silicone-containing copolymer;
 - (c) from 0% to about 1.0% by weight of water; and
 - (d) the balance comprising a carrier suitable for application to hair.
2. A liquid hair cosmetic composition according to Claim 1 wherein the silicone-containing macromer has the general formula (I):



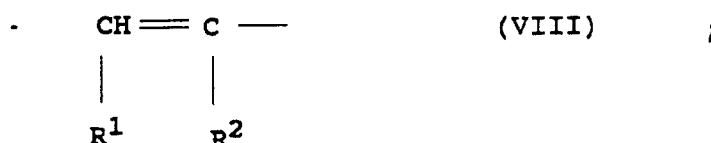
wherein X is a vinyl group; Y is a divalent linking group; R is hydrogen, alkyl, aryl, alkylamino, trialkylsiloxy or alkoxy; Z is a monovalent siloxane polymeric moiety having a number average molecular weight of at least about 500; n is 0 or 1; and m is an integer from 1 to 3.

3. A liquid hair cosmetic composition according to Claim 1 or 2 wherein the silicone-containing copolymer has a weight average molecular weight of from 10,000 to 1,000,000 comprising a hydrophilic carboxylate containing monomer (B), optionally a lipophilic, low polarity, free-radically polymerizable vinyl

monomer (A) which is copolymerizable with B, and a silicone-containing macromer (C) having a weight average molecular weight of from 1,000 to 50,000, preferably from 5,000 to 40,000, based on polydimethylsiloxane and wherein the macromer (C) is selected from one or more monomers having the general formulae (II - VII):



wherein m is 1, 2 or 3; p is 0 or 1; R⁴ is alkyl or hydrogen; q is an integer from 2 to 6; X is



R^1 is hydrogen or $-\text{COOH}$; R^2 is hydrogen, methyl or $-\text{CH}_2\text{COOH}$; Z is



R^4 is alkyl, alkoxy, alkylamino, aryl or hydroxyl; and r is an integer from 5 to 700; and wherein the silicone-containing copolymer comprises from 0% to 98% monomer A, from 1% to 98% monomer B, and from 0.1% to 50% monomer C.

4. A liquid hair cosmetic composition according to any of Claims 1 to 3 wherein the silicone-containing copolymer comprises from 5% to 92% by weight monomer A, from 7.5% to 80% by weight monomer B, and from 0.1% to 50% monomer C.
5. A liquid hair cosmetic composition according to any of Claims 1 to 4 wherein monomer A is selected from acrylic acid esters of C_1 - C_{18} alcohols, methacrylic acid esters of C_1 - C_{18} alcohols, styrene, polystyrene macromer, vinyl acetate, vinyl chloride, vinyl propionate, vinylidene chloride, alpha-methylstyrene, t-butylstyrene, butadiene, cyclohexadiene, ethylene propylene, vinyl toluene, and mixtures thereof; and is preferably selected from n-butylmethacrylate, isobutylmethacrylate, 2-ethylhexylmethacrylate, methylmethacrylate, t-butylacrylate, t-butylmethacrylate, and mixtures thereof.
6. A liquid hair cosmetic composition according to any of Claims 1 to 5 wherein monomer B is selected from acrylic acid, methacrylic acid, maleic acid, maleic anhydride, half esters of maleic anhydride, crotonic acid, itaconic acid and mixtures thereof; and is preferably selected from acrylic acid and methacrylic acid and mixtures thereof.

7. A liquid hair cosmetic composition according to any of Claims 3 to 6 wherein the silicone containing macromer has the general formula (II) in which $p = 0$ and $q = 3$, m is 1, R^4 is alkyl, R^1 is hydrogen and R^2 is methyl.
8. A liquid hair cosmetic composition according to any of Claims 1 to 7 wherein the silicone-containing copolymer is selected from:

acrylic acid/n-butylmethacrylate/polydimethylsiloxane (PDMS) macromer - 20,000 molecular weight (mw) (10/70/20);
acrylic acid/isobutyl methacrylate/PDMS macromer - 20,000 mw (20/60/20 w/w/w)
acrylic acid/PDMS macromer - 20,000 mw (80/20 w/w)
t-butylacrylate(tBA)/acrylic acid(AA)/PDMS macromer - 10,000 mw (60/20/20)
acrylic acid/isobutyl methacrylate/PDMS macromer - 20,000 mw (10/70/20);
acrylic acid/methyl methacrylate/PDMS macromer - 20,000 mw (40/40/20);
acrylic acid/isopropyl methacrylate/PDMS macromer - 20,000 mw (25/65/15);
acrylic acid/methoxyethyl methacrylate/PDMS macromer 20,000 mw (60/25/15);
acrylic acid/PDMS macromer - 20,000 mw (80/20);
and mixtures thereof.
9. A liquid hair cosmetic composition according to any of Claims 1 to 8 wherein the silicone-containing copolymer is neutralised to a level of from about 40% to about 90%, preferably from about 55% to about 85%, more preferably from about 65% to about 80% with sodium hydroxide.
10. A liquid hair cosmetic composition according to any of Claims 1 to 9 containing less than 0.7% by weight water.

11. A liquid hair cosmetic product comprising a hairspray composition and spray dispenser means for containing and spraying the hairspray composition, and wherein the hairspray composition comprises:
- (a) from about 0.1% by weight to about 10% by weight (acid basis) of a silicone-containing polycarboxylic acid copolymer having a vinyl polymeric backbone, and having grafted to the backbone a silicone-containing macromer having a weight average molecular weight of from about 1,000 to about 50,000;
 - (b) a neutralising system consisting essentially of sodium hydroxide present at a level sufficient to neutralise at least about 25% of the acid groups on the silicone-containing copolymer;
 - (c) from 0% to about 1.0% by weight of water; and
 - (d) the balance comprising a carrier suitable for application to hair.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/04756

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :A61K 7/11

US CL :424/70.12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 424/70.12, 70.121, 70.122, DIG1, DIG2

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 4,192,861 (MICCHELLI) 11 March 1980, see abstract, column 2 lines 8-21, column 3 lines 41-62.	1-3, 11
A	US, A, 4,693,935 (MAZUREK) 15 September 1987, see claims 1-13.	1-3, 11

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be part of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 21 JUNE 1995	Date of mailing of the international search report 21 JUL 1995
---	---

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

EDWARD J. WEBMAN

Telephone No. (703) 308-2351

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/04756

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 4-10
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : A61K 7/06, 7/48	A1	(11) International Publication Number: WO 96/32918 (43) International Publication Date: 24 October 1996 (24.10.96)
(21) International Application Number: PCT/US96/04183 (22) International Filing Date: 27 March 1996 (27.03.96) (30) Priority Data: 08/426,332 21 April 1995 (21.04.95) US (71) Applicant: THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventors: TORGERSON, Peter, Marte; 4127 U.S. Route 35 N.W., Washington Courthouse, OH 43160 (US). DANZIGER, James, Lee; 9556 Parrot Place, Mason, OH 45040 (US). (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).		(81) Designated States: AU, BR, CA, CN, JP, KR, MX, TR, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: TOPICAL PERSONAL CARE COMPOSITION CONTAINING ALKENYL OR STYRENE END-CAPPED SILICONE GRAFTED COPOLYMER		
(57) Abstract Topical personal care compositions containing aqueous or hydroalcoholic carriers and silicone grafted copolymers with acid-containing monomers characterized by substantially improved or eliminated hydrolysis of the silicone portion of the copolymer are obtained by the selection of specific types of silicone macromers for incorporation into the silicone grafted copolymer. The silicone macromers are selected from the group consisting of alkenyl end-capped silicone macromers and styrene end-capped silicone macromers, and combinations thereof. The silicone macromers are ethylenically unsaturated, polymerizable monomers having a styrene or alkenyl end-capped silicone group covalently bound to the ethylenically unsaturated portion of the monomer via the styrene or alkenyl end-cap.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

TOPICAL PERSONAL CARE COMPOSITION CONTAINING ALKENYL OR STYRENE END-CAPPED SILICONE GRAFTED COPOLYMER

5

TECHNICAL FIELD

This invention relates to topical personal care compositions containing silicone grafted copolymers and an aqueous or hydroalcoholic carrier suitable for application to the skin or hair, wherein the silicone grafted copolymer is soluble or dispersible in the continuous phase of the carrier.

BACKGROUND OF THE INVENTION

The use of silicone grafted copolymers in a wide variety of topical care compositions, e.g. hair and skin care compositions, has become widely known. These polymers are useful for their film forming and adhesive properties, they can be used as adhesive agents in hair sprays, mousses, and lotions, as well as for a wide variety of skin care products such as cosmetics and skin conditioning compositions, wherein their film forming properties are used to smooth the skin or as an aid to deliver other ingredients to the skin. One of the primary benefits of silicone grafted copolymers is that the silicone portions provide improved tactile properties relative to conventional polymers. For example, hair treated with them retains its styled shape in accordance with the wishes of the user, yet feels softer than hair styled with conventional hair styling polymers. Skin treated with silicone grafted polymers feels smoother to the touch than skin treated with conventional polymers.

One of the most desirable and least costly ways to use silicone grafted copolymers is to formulate them into aqueous or hydroalcoholic carriers, wherein the silicone grafted copolymers is soluble in or otherwise stably distributed throughout the aqueous/hydroalcoholic phase. An alternate and also desirable type of composition provides the silicone grafted copolymer solubilized in a nonaqueous solvent, such as cyclomethicone or a hydrocarbon, which is emulsified in the form of droplets distributed throughout the aqueous or hydroalcoholic carrier. Whereas this type of formulation is useful and desirable for many types of products, it is more desirable and less expensive for many other products to use silicone grafted copolymers that are solubilized or stably dispersed in non-emulsified, non-droplet form in the aqueous or hydroalcoholic carrier.

One of the preferred types of silicone grafted copolymers for use in aqueous topical personal care compositions, especially hair spray compositions, contains

acrylic acid monomers and methacryloxy propyl end-capped silicone macromers. It is highly desirable to use acrylic acid monomers because the acid group provides a high degree of polarity which allows the polymer to be soluble or dispersible in water or hydroalcoholic carriers. Other highly polar monomers, such as many cationic
5 monomers, can provide similar solubility to the polymer but tend to be more hygroscopic. This can result in the product becoming sticky during use, particularly during humid conditions. Unfortunately, it has been found that these silicone grafted copolymers tend to hydrolyze in the aqueous or hydroalcoholic products at an undesirably high rate, resulting in separation of the silicone portion from the
10 remainder of the copolymer. Similar copolymers containing the same type of silicone macromer but not containing the acrylic acid monomer do not hydrolyze at such high rates. Therefore, it appears that the hydrolysis problem surprisingly only occurs when the polymer contains an acrylic acid or other acid-containing monomer.

Hydrolysis is of concern since a wide variety of products contain water as the
15 primary or cosolvent for hair styling polymers and other hair and skin care adhesive polymers. It is a particularly concerning issue in view of the current trend toward developing products having high water content and reduced levels of volatile organic compounds (VOC's). Of particular interest is the trend toward regulation of product to contain reduced levels of VOC's, such as the 55% and 80% VOC regulations
20 anticipated or already present in numerous countries. As the trend toward topical personal care products with reduced levels of VOC's continues, VOC-based formulas will be replaced in whole or in part with aqueous and hydroalcoholic formulas.

It is an object of this invention to provide aqueous and hydroalcoholic topical personal care compositions containing silicone grafted copolymers which have
25 improved stability against hydrolysis. It is also an object of this invention to provide compositions as described above which contain acrylic acid or other acid-containing monomers in the silicone grafted copolymer, or which otherwise can provide the product attributes found in such copolymers. It is another object of this invention to provide compositions which meet the above objects and which contain relatively low
30 or zero levels of volatile organic compounds. These and other benefits of the present invention as may be or become apparent to those in the art can be obtained by the invention described below.

Unless otherwise indicated, all percentages are calculated by weight of the total composition and all ratios are calculated on a weight basis. Unless otherwise
35 indicated, ingredient amounts are based on the active level and therefore do not include carriers or by-products that may be included in commercial or otherwise available materials. The present invention may comprise, consist of, or consist

essentially of any of the essential and various optional and/or preferred ingredients and elements described herein. The terms "soluble" and "insoluble" shall refer to the solubility characteristics of a particular ingredient in the composition, unless otherwise specifically indicated. All viscosities and solubilities are determined at 25°C, unless otherwise specifically indicated. Also, unless otherwise indicated, all weight percentages of the compositions hereof are based on the total weight of the composition exclusive of any propellant that may be possibly incorporated into the product or otherwise contemplated.

SUMMARY OF THE INVENTION

Topical personal care compositions containing aqueous or hydroalcoholic carriers and silicone grafted copolymers characterized by substantially improved or eliminated hydrolysis of the silicone portion of the copolymer can be obtained in accordance with the present invention. It has been found that such compositions can be obtained by combining acid-containing monomers with the selection of specific types of silicone macromers for incorporation into the silicone grafted copolymer. The silicone macromers hereof are selected from the group consisting of alkenyl end-capped silicone macromers and styrene end-capped silicone macromers, and combinations thereof. The silicone macromers are ethylenically unsaturated, polymerizable monomers having a styrene or alkenyl end-capped silicone group covalently bound to the ethylenically unsaturated portion of the monomer via the styrene or alkenyl end-cap.

The compositions hereof can be used in a wide variety of topical personal care applications, including hair care, skin care, cosmetics, and personal cleansing compositions. They are especially useful for hair styling products, such as hair sprays, hair lotions, hair tonics, mousses, hair rinses, and shampoos. Other useful, specific product applications include skin care compositions such as skin moisturizers and other skin conditioning compositions, sunscreens, sunless tanning compositions, skin cleansing compositions, anti-acne compositions, topical analgesic compositions, and other drug-containing topical skin compositions. Skin care compositions also include cosmetics.

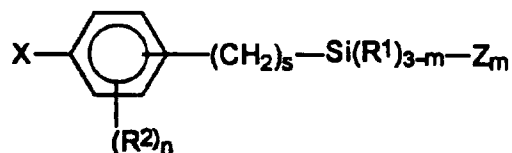
More specifically, the present invention provides topical personal care compositions containing silicone grafted copolymer having improved resistance against hydrolysis, wherein the compositions comprise:

- (a) from about 0.1% to about 50%, by weight of the composition, of silicone grafted copolymer containing:
 - (i) from about 1% to about 99%, by weight of the copolymer, of acid-containing monomers, said acids of the acid-containing monomers

preferably being selected from the group consisting of carboxylic acid and sulfonic acid, and combinations thereof;

(ii) from about 1% to about 50% of silicone macromers having the formula:

5

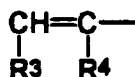


or



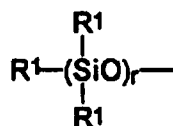
10

wherein: s is an integer from 0 to about 6; m is an integer from 1 to 3, R² is C1-C10 alkyl or C7-C10 alkylaryl; n is an integer from 0 to 4; X is an ethylenically unsaturated group of the formula :



15

wherein R³ is -H or C1-C6 alkyl; R⁴ is H or C1-C6 alkyl; Z is



20

wherein each R¹ independently is an alkyl, aryl or alkylaryl having from 1 to 10 carbon atoms, and r is an integer from about 4 to about 700, and combinations thereof;

(iii) from 0% to about 98% of additional monomers, and combinations thereof; and

25

(b) from about 1% to about 99.9%, by weight of the composition, of an aqueous or hydroalcoholic solvent for said silicone grafted copolymer suitable for application to the hair or skin, wherein said copolymer is soluble or dispersible in said solvent.

The present invention is described in more detail below in the Detailed Description of the Invention.

DETAILED DESCRIPTION OF THE INVENTION

The topical personal care compositions of the present invention generally comprise: (a) from about 0.1% to about 50%, by weight, of the styrene or alkenyl end-capped silicone grafted copolymer hereof, preferably from about 0.2% to about 20%, more preferably from about 0.5% to about 15%, even more preferably from about 1% to about 10%, most preferably from about 2% to about 8%; and (b) from about 1% to about 99.9%, by weight, of an aqueous or hydroalcoholic solvent for the silicone grafted copolymer suitable for application to the hair or skin, preferably from about 50% to about 99.8%, more preferably from about 60% to about 99.5%, even more preferably from about 70% to about 99%, most preferably from about 80% to about 98%. The silicone grafted copolymer is soluble or dispersible in the aqueous or hydroalcoholic solvent.

The topical personal care compositions hereof are, by definition, suitable for topical application to the skin or hair. By "suitable for topical application to the skin or hair" what is meant that the compositions are safe for topical application to the skin or hair when used in their intended manner and effective for delivering the copolymers hereof to the skin or hair in such a manner that the copolymer can provide its intended benefit.

Aqueous or Hydroalcoholic Solvent

The aqueous or hydroalcoholic solvent for the copolymers of the present invention can be water or a combination of water and one or more monohydric C1-C6 alcohols, preferably C2-C3 alcohols, more preferably C2 alcohol (i.e., ethanol). The levels of total aqueous or hydroalcoholic solvent are described above. By hydroalcoholic, what is meant is any mixture of water and one or more of the alcohols containing at least about 0.5%, by weight of the solvent, of water.

For hair care products in general, such as hair sprays and mousses, however, the compositions hereof will generally comprise at least about 5% water, preferably at least about 10% water, more preferably at least about 20% water.

In another aspect of this invention, the compositions hereof are characterized by reduced levels of volatile organic compounds (VOC's), and will comprise from about 40% to about 99.9% water and from 0% to about 80% of the monohydric alcohols, preferably from 0% to about 55% of the monohydric alcohols. In a particularly preferred embodiment for aerosol or nonaerosol hairspray compositions, the compositions will comprise from about 40% to about 75% water and from about 20% to about 55% monohydric alcohol, or from about 40% to about 95% water and from 0% to about 55% monohydric alcohol. In reduced VOC compositions, the total level of VOC's will preferably be no greater than about 80%, by weight of the composition, inclusive of propellants, preferably no greater than about 55%.

For purposes hereof, VOC's are defined as any organic compounds (including silicones) which either have: a vapor pressure at 20°C of 0.1 mm Hg or higher; or contain 12 or less carbon atoms. Conversely, organic compounds having a vapor pressure of less than 0.1 mm Hg under the same conditions or which contain more than 12 carbon atoms are defined herein as being nonvolatile.

The styrene and alkenyl end-capped silicone grafted copolymers hereof are soluble or dispersible in the aqueous or hydroalcoholic solvent. This is in contrast to the situation wherein the copolymer is not soluble or dispersible in the solvent, thereby existing in a separate or discontinuous phase from the solvent.

Additional solvents, cosolvents, and solubilizing aids may be incorporated into the compositions hereof to assist with solubilization of the copolymer without departing from the spirit or intent of the invention. Examples of such ingredients include, but are not limited to, di- and tri- hydric alcohols, surfactants and emulsifiers.

Styrene/Alkenyl End-Capped Silicone Grafted Copolymer

The silicone grafted copolymer (hereinafter sometimes referred to as "the copolymer") constitutes an essential component of the present invention. The term "copolymer", as used herein, refers to polymers derived by polymerization of two or more different species of monomers. The copolymers hereof are made by the copolymerization of one or more types of acid-containing monomers, one or more species of certain styrene or alkenyl end-capped silicone macromers (or a mixture thereof), and optionally one or more other types of monomers. For convenience, the copolymers hereof may sometimes be referred to as being derived from said monomers and macromers, meaning that the copolymer is made by copolymerization of said monomers and macromers. The term "monomer", as used herein, means ethylenically unsaturated compounds capable of being polymerized to form copolymers, as defined herein. The term "macromer", as used herein, shall refer to a monomer characterized by having a polymeric substituent. The essential macromers of the present invention are silicone macromers, meaning that the macromers have silicone as a polymeric substituent. Also, the copolymers hereof may sometimes be said to comprise said monomers and macromers, meaning that the copolymer comprises units corresponding to the indicated pre-polymerization monomers and macromers.

Acid-Containing Monomers

The copolymers hereof comprise from about 1% to about 99%, by weight of the copolymer, of acid-containing monomers. In general, the copolymers will preferably comprise from about 5% to about 90%, more preferably from about 10%

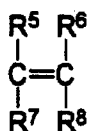
to about 80%, most preferably from about 15% to about 75%. The particular level of acid-containing monomer preferred for any specific composition can vary depending on the type of formulation and intended use, as well as the types and amounts of the other monomers and macromers in the copolymer and the molecular weight of the copolymer. For hair spray and other hair care compositions, for example, the copolymer preferably comprises from about 5% to about 50%, by weight of the copolymer, of acid-containing monomer, more preferably from about 10% to about 35%, most preferably from about 15% to about 25%.

The acid-containing monomers will preferably be selected from monomers containing acid groups selected from the group consisting of carboxylic acids and sulfonic acids, most preferably carboxylic acids. Other acid-containing monomers can also be used, including but not limited to phosphonic acid-containing monomers. Combinations of the above types of acid-containing monomers can also be used.

The acid-containing monomer units present in the final copolymer can be derived from polymerizable acid-containing starting monomers, or from polymerizable nonionic monomers which are modified subsequent to polymerization to the acid functionalities. Included within the term acid-containing monomers are the neutralized versions, i.e. salts, of the monomers hereof. Neutralization is discussed in more detail below.

Examples of acid-containing monomers include:

(i) Carboxylic acid-containing monomers, including those corresponding to the formula:



wherein: R^5 and R^6 independently are H or C1-C6 alkyl, preferably H or methyl; R^7 is H, C1-C6 alkyl, or a carboxylic moiety having up to about 12 carbon atoms, preferably H or methyl, or if R^7 is a carboxylic acid moiety, preferably acrylic acid; and R^8 is a carboxylic moiety having up to about 12 carbon atoms.

Specific examples of carboxylic acid-containing monomers include acrylic acid, methacrylic acid, maleic acid, maleic acid half ester, itaconic acid, fumaric acid, and crotonic acid, half esters of polybasic acid anhydride such as succinic anhydride, phthalic anhydride or the like reacted with a hydroxyl group-containing acrylate and/or methacrylate such as hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxypropyl acrylate, and the like.

(ii) Sulfonic acid-containing monomers such as styrenesulfonic acid, and sulfoalkyl acrylates and methacrylates, preferably with C1-C6 alkyl groups, more preferably C2 alkyl groups, such as sulfoethyl acrylate, sulfoethyl methacrylate, and the like.

5 (iii) Phosphoric acid-containing monomers such as the phospho oxyalkyl acrylates and methacrylates, preferably with C1-C6 oxyalkyl groups, more preferably C1-C3 oxyalkyl. Specific examples include phospho-oxyethyl acrylate, phospho-oxyethyl methacrylate, 3-chloro-2-acid phospho-oxypropyl acrylate, phospho-oxypropyl methacrylate, and the like.

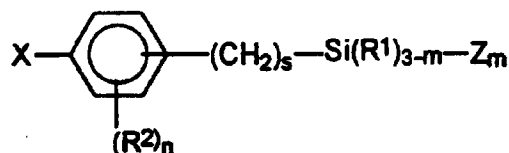
10 Preferred acid containing monomers are the carboxylic acids and the sulfonic acids. Most preferred are the carboxylic acids. Examples of highly preferred acid-containing monomers are acrylic acid, methacrylic acid, and styrenesulfonic acid. Especially preferred acid-containing monomers are acrylic acid and methacrylic acid.

Styrene and Alkenyl End-Capped Silicone Macromers

15 The copolymers hereof comprise from about 1% to about 50%, by weight of the copolymer, of styrene end-capped silicone macromers, alkenyl end-capped silicone macromers, or a combination thereof, preferably from about 2% to about 40%, more preferably from about 5% to about 40%, most preferably from about 5% to about 25%. By "styrene" or "alkenyl" end-capped silicone macromer what is
20 meant is that the macromer contains a silicone, i.e. polymeric siloxane or "polysiloxane" group, that is covalently bound to the monomer via a styrene group or an alkenyl group, respectively.

The preferred styrene end-capped silicone macromers and alkenyl end-capped macromers of the present invention have the formulas, respectively:

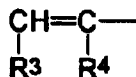
25



and

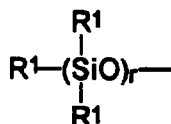


30 wherein: s is an integer from 0 to about 6, preferably 0, 1, or 2, more preferably 0 or 1; m is an integer from 1 to 3, preferably 1; R² is C1-C10 alkyl or C7-C10 alkylaryl, preferably C1-C6 alkyl or C7-C10 alkylaryl, more preferably C1-C2 alkyl; n is an integer from 0 to 4, preferably 0 or 1, more preferably 0; X is an ethylenically unsaturated group (prior to polymerization) of the formula:



wherein R^3 is H or C1-C6 alkyl, preferably H or C1-C2 alkyl, more preferably H; R^4 is H or C1-C6 alkyl, preferably H or C1-C2 alkyl, more preferably H or methyl; Z is:

5



wherein: each R^1 independently is an alkyl, aryl or alkylaryl having from 1 to 10 carbon atoms, preferably C1-C6 alkyl, more preferably C1-C2 alkyl, most preferably methyl; and r is an integer from about 4 to about 700, preferably from about 50 to about 500, more preferably from about 100 to about 300; and combinations thereof. For hair care compositions, such as hair sprays, r is most preferably from about 150 to about 200. The styrene end-capped silicone macromers are preferred.

The silicone portion of the macromer is preferably substituted at the para or meta positions of the aromatic ring relative to X, most preferably at the para position. If n is not 0, then the R^2 group or groups are preferably substituted at the meta positions. The ortho positions are preferably, but not necessarily, unsubstituted.

Styrene and alkenyl end-capped silicone macromers and methods for making them are well-known in the art. See, for example, Holohan, George, Barrie, and Parker, "Monofunctional Polydimethylsiloxane Oligomers For Graft Copolymerization", *Macromol. Chem. Phys.* 195, 2965-2979 (1994), which discloses silicone macromers wherein $s = 0$ for styrene end-capped macromers and wherein $s = 0$ or an integer for alkenyl end-capped silicone macromers. Further disclosure relating to methods of making the silicone macromers hereof can be found in the Experimental section, below.

25 Additional Monomers

The copolymers hereof, in general, comprise from 0% to about 98%, by weight of the copolymer, of additional monomers other than the acid-containing monomers and styrene or alkenyl end-capped silicone macromers described above, preferably from 0% to about 80%, more preferably from 20% to about 70%. For hair care compositions, such as hair sprays, the copolymer preferably comprises from 40% to about 70% of additional monomers. The use of additional monomers can be especially desirable for increasing the T_g of the copolymer, as described in more detail below, or for adjusting the solubility of the copolymer, depending upon the

particular types and levels of the other copolymers and the type and amount of the aqueous or hydroalcoholic solvent. When used in whole or part for one or both of these purposes, the additional monomers will generally be used at a level of at least about 1%, by weight of the copolymer, more generally at least about 2%, preferably at least about 5%, more preferably at least about 10%.

A wide variety of the additional monomers can be used. These include nonionic monomers, cationic monomers, and amphoteric monomers. The nonionic monomers can be either low or high polarity monomers. The cationic monomers can be polymerized in the cationic state, or can be polymerized as a nonionic precursor which is then quaternized or otherwise made cationic subsequent to polymerization. If cationic monomers are to be used, it is preferred that the weight percentage of at least one of either the cationic or acid-containing monomers be no greater than about 10%, preferably no greater than about 5%, to minimize the occurrence of ionic interaction between the two charged groups.

Examples of low polarity nonionic monomers are: acrylic and methacrylic acid esters of C1-C24 alcohols, such as methanol, ethanol, allyl alcohol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 1-methyl-1-butanol, 3-methyl-1-butanol, 1-methyl-1-pentanol, 2-methyl-1-pentanol, 3-methyl-1-pentanol, t-butanol, cyclohexanol, 2-ethyl-1-butanol, 3-heptanol, benzyl alcohol, 2-octanol, 6-methyl-1-heptanol, 2-ethyl-1-hexanol, 3,5-dimethyl-1-hexanol, 3,5,5-trimethyl-1-hexanol, 1-decanol, 1-dodecanol, 1-hexadecanol, 1-octadecanol, oleyl alcohol, isobornyl alcohol, tetrahydrofurfuryl alcohol, and the like, the alcohols preferably having an average number of carbon atoms of from about 1-18, more preferably from about 1-12; styrene; alkylstyrenes, preferably with C1-C6 alkyls, such as t-butylstyrene; chlorostyrene; vinyl esters such as vinyl acetate and vinyl propionate; vinyl chloride; vinyl toluene; vinyl caprolactam; vinylidene chloride; acrylonitrile; alpha-alkylstyrenes, preferably with C1-C6 alkyl groups, such as alpha-methylstyrene; 1,3-dialkenes, such as butadiene and cyclohexadiene; ethylenically unsaturated hydrocarbons, preferably C1-C5 alkenes, such as ethylene and propylene; alkoxyalkyl (meth)acrylates, preferably with C1-C6 alkyl groups, such as methoxy ethyl (meth)acrylate, butoxyethyl (meth)acrylate; and alkyl vinyl ethers, preferably C1-C6 alkyl vinyl ethers, such as methyl vinyl ether. Other low polarity nonionic monomers include: acrylate and methacrylate derivatives such as di-acrylates and di-methacrylates, e.g. ethylene glycol di-acrylate, ethylene glycol di-methacrylate, 1,3-butyleneglycol di-acrylate and -methacrylate; and

diacetonacrylamide. As used herein, the clause "(meth)acrylate" shall mean that both "acrylate" and "methacrylate" are disclosed.

Preferred low polarity nonionic monomers include n-butyl methacrylate, isobutyl methacrylate, 2-ethylhexyl methacrylate, methyl methacrylate, t-butylacrylate, t-butylmethacrylate, and mixtures thereof.

Exemplary high polarity nonionic monomers include; acrylamide; methacrylamide; N,N-dialkyl(meth)acrylamides, especially with C1-C6 alkyls, preferably methyl, such as N,N-dimethylacrylamide; N-alkyl acrylamides, especially with C1-C6 alkyls, such as N-t-butyl acrylamide and isopropylacrylamide; acrylate and methacrylate alcohols, especially C2-C6 (meth)acrylate alcohols, such as hydroxyethyl acrylate, hydroxyethylmethacrylate, hydroxypropylacrylate, and hydroxypropylmethacrylate; vinyl pyrrolidone, allyl alcohol, and vinyl alcohol (made by hydrolyzing vinyl acetate after polymerization).

Cationic monomers include quaternizable, amino-functional, ethylenically unsaturated monomers, such as the amino functional derivatives of styrene, acrylamide, methacrylamide, (meth)acrylates such as the C₁-C₅ alkyl esters of acrylic acid and methacrylic acid. Preferred are C₁-C₅ alkyl amines especially C₁-C₃ amines. It is preferred to use the tertiary amines. (e.g., trialkyl amines), though it is not meant to necessarily exclude monoalkyl amines, dialkyl amines, and other alkyl amine derivatives. Especially preferred are dimethyl amino C₁-C₃ alkyl amines. These monomers can be quaternized prior to or subsequent to polymerization, preferably subsequent to polymerization.

Cationic monomers include:

(i) monomers derived from acrylic acid or methacrylic acid, which is referred to hereinafter collectively as (meth)acrylic acid, and a quaternarized epihalohydrin product of a trialkylamine having 1 to 5 carbon atoms in the alkyl such as (meth)acryloxypropyltrimethylammonium chloride and (meth)acryloxypropyltriethylammonium bromide;

(ii) amine derivatives of (meth)acrylic acid or amine derivatives of (meth)acrylamide derived from (meth)acrylic acid or (meth)acrylamide and a dialkylalkanolamine having C1-C4 alkyl groups such as dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, dimethylaminopropyl (meth)acrylate, or dimethylaminopropyl (meth)acrylamide; and

(iii) derivatives of the products of the group (ii) above by (1) neutralization with an acid such as hydrochloric acid, or lactic acid, (2) modification with a halogenated alkyl, such as methyl chloride, ethyl chloride, methyl bromide, or

ethyl iodide, (3) modification with a halogenated fatty acid ester such as ethyl monochloroacetate, or methyl monochloropropionate, and (4) modification with a dialkyl sulfate such as dimethyl sulfate, or diethyl sulfate.

Specific examples of such monomers include: (i) p-dimethylaminomethyl
5 styrene, p-dimethylaminoethyl styrene; (ii) dimethylaminomethyl acrylamide, dimethylaminopropyl acrylamide, dimethylaminopropyl methacrylamide, dimethylaminomethyl methacrylamide; dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, dimethylaminopropyl (meth)acrylate, and dimethylaminopropyl (meth)acrylamide. Cationic monomers also include amine
10 derivatives of allyl compounds such as diallyldimethylammonium chloride and the like.

As discussed above, cationic monomers can be polymerized in cationic form, or as an alternative they can be polymerized in the form of their precursors, which are then modified to be cationic, for example, by a quaternizing agent (e.g.
15 ethyl monochloroacetate, dimethyl sulfate, etc.).

Examples of the amphoteric monomers include zwitterionized derivatives of the aforementioned amine derivatives of (meth)acrylic acids or the amine derivatives of (meth)acrylamide such as dimethylaminoethyl (meth)acrylate, dimethylaminopropyl(meth)acrylamide by a halogenated fatty acid salt such as
20 potassium monochloroacetate, sodium monobromopropionate, aminomethylpropanol salt of monochloroacetic acid, triethanolamine salts of monochloroacetic acid and the like; and amine derivatives of (meth)acrylic acid or (meth)acrylamide, as discussed above, modified with propanesultone.

These amphoteric monomers, like the aforementioned cationic monomers,
25 can be polymerized in amphoteric form or, as an alternative, they can also be polymerized in the form of their precursors, which are then converted into the amphoteric state.

Copolymers

The copolymers hereof should have a weight average molecular weight of at
30 least about 20,000, for purposes of providing effective adhesive or film forming properties upon application to the hair or skin. There is no upper limit for molecular weight except that which limits applicability of the invention for practical reasons, such as processing, aesthetic characteristics, formulateability, etc. In general, the weight average molecular weight will be less than about
35 10,000,000, more generally less than about 5,000,000, and preferably less than about 3,000,000. Preferably, the weight average molecular weight will be between about 50,000 and about 2,000,000, more preferably between about

75,000 and about 1,000,000, most preferably between about 100,000 and about 750,000. Molecular weight can be determined by gel permeation chromatography via universal calibration with refractive index and differential viscometric detection using polystyrene standards, or equivalent.

- 5 Preferably, the copolymer hereof when dried to form a film has a Tg of at least about -20°C, preferably at least about 20°C, so that they are not unduly sticky, or "tacky" to the touch. Preferably, the Tg is from about 20°C to about 120°C. As used herein, the abbreviation "Tg" refers to the glass transition temperature of the non-silicone backbone of the copolymer. Tg can be measured
10 by techniques well known in the art, such as by differential scanning calorimetry (DSC) or dynamic mechanical analysis. Tg can be controlled by varying the level and type of the various acid-containing monomers and additional monomers that are used.

- Methods for making silicone grafted copolymers have become well-known
15 in the published art. The present silicone grafted copolymers can be made in accordance with known processes, subject to the additional requirement that the starting monomers be chosen such that the final product will be constituted of acid-containing monomers and styrene end-capped silicone macromers as described above. Examples of processes for making silicone grafted polymers are
20 described in detail in U.S. Patent 4,693,935, Mazurek, issued September 15, 1987, and U.S. Patent 4,728,571, Clemens et al., issued March 1, 1988, both of which are incorporated herein by reference, and also in U.S. Patent 5,061,481, Suzuki et al., issued October 29, 1991, U.S. Patent 5,219,560, Suzuki et al., issued June 15, 1993, U.S. Patent 5,166,276, Hayama et al., issued November 24, 1992, U.S. Patent
25 5,106,609, Bolich et al., issued April 21, 1992, U.S. Patent 5,100,658, Bolich et al., issued March 31, 1992, U.S. Patent 5,100,657, Ansher-Jackson et al., issued March 31, 1992, U.S. Patent 5,104,646, Bolich et al., issued April 14, 1992, EPO 0 412 707, Torgerson et al., granted February 4, 1994, EPO 0 412 704, Bolich et al., published February 13, 1991, EPO application 92918969.4, Peffly, filed August 18,
30 1992, EPO Application 92918839.9, Hozshuh, et al., filed August 18, 1992, and EPO Application 92919224.3, filed August 18, 1992, all of which are incorporated herein by reference.

- In general, the copolymers of the present invention can be made by free radical polymerization of silicone macromers with acid-containing monomers and
35 other monomers that may be used. The general principles of free radical polymerization methods are well understood. See, for example, Odian, "Principles of Polymerization", 2nd edition, John Wiley & Sons, 1981, pp. 179-

318. The desired monomers are all placed in a reactor, along with a sufficient amount of a mutual solvent so that when the reaction is complete the viscosity of the reaction is reasonable. Typical monomer loadings are from about 20% to about 50%. Undesired terminators, especially oxygen, are removed as needed.

5 This can be done by evacuation or by purging with an inert gas, such as argon or nitrogen. The initiator is introduced and the reaction brought to the temperature needed for initiation to occur, assuming thermal initiators are used. Alternatively, redox or radiation initiation can be used as desired. The polymerization is allowed to proceed as long as needed for a high level of conversion to be achieved,

10 typically from a few hours to a few days. The solvent is then removed, usually by evaporation or by precipitating the copolymer by addition of a nonsolvent. The polymer is further purified, as needed.

The copolymers hereof will preferably be utilized in at least partially neutralized form. Neutralization can promote solubility or dispersibility of the polymer in the composition. In addition, use of the neutralized form aids in

15 removability of the copolymer from the hair or skin upon cleansing with shampoo, soap, detergent, or other cleansing product. In general, it is preferred that from about 10% to 100%, more preferably from about 20% to about 90%, even more preferably from about 40% to about 85%, of the acidic functionality of the polymer be neutralized.

20

Any conventionally used base, organic or metallic, may be used for neutralization. Hydroxides of alkali metal and alkaline earth metal are suitable neutralizers for use with the silicone grafted copolymers. Preferred neutralizing agents for use in hair spray compositions of the present invention are potassium

25 hydroxide and sodium hydroxide. Examples of other suitable neutralizing agents which may be used include amines, especially amino alcohols such as 2-amino-2-methyl-1,3-propanediol (AMPD), 2-amino-2-ethyl-1,3-propanediol (AEPD), 2-amino-2-methyl-1-propanol (AMP), 2-amino-1-butanol (AB), monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), mono-isopropanolamine (MIPA), diisopropanol-amine (DIPA), triisopropanolamine (TIPA) and dimethyl steramine (DMS). Mixtures of amines and bases (metallic or organic) may also be used.

30

Removal of unreacted silicone macromer, if any is present at undesirably high levels which can interfere with product performance, can be done by any

35 means known in the art. One method that can be used is supercritical fluid extraction, such as with supercritical carbon dioxide. Another generally

applicable method is membrane separation, performed in accordance with standard techniques of the art.

A purification method which can be particularly useful for the copolymers hereof is solvent extraction with a nonpolar solvent. Suitable solvents include C3-
5 C8 hydrocarbons, preferably C5-C6 hydrocarbons, such as hexane. Before performing the extraction, the polymer reaction product is precipitated out of the reaction solvent (e.g., with water), and dried. The extraction solvent is preferably heated to near or slightly above the average Tg of the non-silicone backbone portion of the polysiloxane-grafted polymer of the adhesive agent. The
10 temperature should be high enough so that the polymer softens, but not so high such that it congeals. The extraction solvent and reaction product can be mixed before, or after heating the solvent. The extraction solvent and polymer reaction product should be held with mixing and preferably in an excess of solvent, for a reasonable period to effectuate removal of the soluble materials. This period will
15 depend upon the reflux temperature of the solvent, the Tg of the copolymer, the temperature to which the solvent is actually heated, the desired level of removal of unreacted monomer and low viscosity material remaining after polymerization, and the number of cycles of solvent extraction to be performed. Typically, the solvent extraction periods will be from about one-half hour to about two hours,
20 more typically from about one-half hour to about one hour. The solvent can be removed after each cycle by conventional means, e.g., decanting, filtering, etc., with drying or distillation to remove trace extraction solvent remaining in the product after the final extraction cycle.

Analysis of the polymer reaction product and the extracted materials, and
25 the purified film-forming agent can be done by conventional analysis techniques known in the art. These include, for example, nuclear magnetic resource (NMR), infrared molecular spectroscopies, gel permeation/size exclusion chromatography, liquid chromatography, gas chromatography, atomic absorption and emission spectroscopies, and wet methods such as titration.

30 Topical Personal Care Compositions

A wide variety of topical personal care compositions are contemplated under the present invention, including both hare care compositions and skin care compositions. Hair care compositions include hair sprays (aerosol and nonaerosol), hair tonics, hair lotions, shampoos, hair rinses, and mousses. Skin
35 care compositions include skin moisturizers and other skin conditioning compositions, sunscreens, sunless tanning compositions, skin cleansing compositions, anti-acne compositions, topical analgesic compositions and other

drug-containing topical skin applications, and the like. Skin care compositions also include cosmetics and fragrances, especially those intended for use in the facial area. Cosmetics include, for example: foundations; eye make-up, such as mascara; and lip make-up. Fragrances include perfumes, colognes, and after-shaves.

Topical personal care compositions of the present invention include products wherein the copolymer is used as an adhesive to style hair, to modify the surface of the skin for skin conditioning purposes or for cosmetic appearance purposes. The copolymer hereof can also be used to facilitate delivery of an active ingredient to the hair or skin. Substantivity to the skin or hair can be enhanced for such ingredients as a result of entrapment by the adhesive films the copolymers of the present invention can form upon curing. Examples of such active ingredients include drugs, cosmetic actives (e.g., hair or skin conditioners, dyes and pigments for cosmetics, perfumes and fragrances, and the like), sunscreen actives (including physical sun-blocking actives such as zinc or titanium dioxide, as well as chemical sunscreens which protect the skin or hair by selective absorption of UV-A and/or UV-B rays), and sunless tanning agents.

The compositions hereof can be formulated to include any of the ingredients typically known for use in the type of product that is desired, as well as any other ingredients that may provide desirable benefits without interfering unduly with the function of the styrene end-capped silicone grafted copolymer hereof. A nonexclusive description of a variety of such ingredients for use in topical personal care compositions is provided below.

The topical personal care compositions can contain a wide variety of volatile materials including, but not limited to acetone, hydrocarbons (such as isobutane, hexane, decene), halogenated hydrocarbons (such as Freons), linalool, esters (such as ethyl acetate, dibutyl phthalate), and volatile silicon derivatives (especially siloxanes such as phenyl pentamethyl disiloxane, methoxypropyl heptamethyl cyclo-tetrasiloxane, chloropropyl pentamethyl disiloxane, hydroxypropyl pentamethyl di-siloxane, cyclomethicones such as octamethyl cyclotetrasiloxane and decamethyl cyclopentasiloxane, and polydimethyl siloxanes, such as dimethicone having, for example, a viscosity at 25°C of about 15 centipoise or less), and mixtures thereof. Volatile materials such as these are commonly used in topical compositions, such as sprays, tonics, gels, and mousses.

Aerosol topical personal care compositions, such as mousses and aerosol hair sprays, can utilize any of the conventional propellants to deliver the material. Examples of suitable propellants include materials such as trichlorofluoromethane,

dichlorodifluoromethane, difluoroethane, dimethylether, propane, n-butane or isobutane. Aerosol as well as nonaerosol spray products may include a surfactant to enhance spray quality. Examples of suitable surfactants include nonionic, cationic, anionic surfactants, or mixtures thereof. Fluorosurfactants are also encompassed
5 herein. Surfactants are particularly desirable for the spray product of the present invention, especially spray products such as hair spray, wherein the spray quality can affect product performance, since the compositions hereof have relatively low levels of volatile organic compounds and relatively high levels of water. The high water levels of the present compositions can otherwise adversely affect spray quality. If
10 such a surfactant is used, it is preferably present at a level of from about 0.01% to about 7.5% by weight of the total composition. The level of propellant can be adjusted as desired. It is generally from about 3% to about 30% by total weight of the composition (weight basis inclusive of propellant) of mousse compositions and from about 15% to about 50% of the aerosol hair spray compositions. The
15 propellant level in other product forms may vary widely, but is generally between about 3% and about 70%, by weight of the total composition.

Suitable spray containers are well known in the art and include conventional, non-aerosol pump sprays i.e., "atomizers," aerosol containers or cans having propellant, as described above, and also pump aerosol containers utilizing
20 compressed air as the propellant. Pump aerosol containers are disclosed, for example, in U.S. Patents 4,077,441, March 7, 1978, Olofsson and 4,850,577, July 25, 1989, TerStege, both incorporated by reference herein, and also in U.S. Serial No. 07/839,648, Gosselin, Lund, Sojka, and Lefebvre, filed February 21, 1992, "Consumer Product Package Incorporating A Spray Device Utilizing Large Diameter
25 Bubbles. Pump aerosols hair sprays using compressed air are also currently marketed by The Procter & Gamble Company under their tradename VIDAL SASSOON AIRSPRAY^R hair sprays.

The compositions of the present invention can be in a wide variety of forms. For example, single phase compositions as well as emulsions wherein the silicone
30 grafted copolymer is present in the aqueous or hydroalcoholic phase of the emulsion. Exemplary emulsions include, but are not limited to, oil-in-water, water-in-oil, water-in-oil-in-water, and oil-in-water-in-silicone emulsions. The silicone grafted copolymer hereof will be present in an aqueous or hydroalcoholic phase of the composition.

35 The compositions can cover a broad range of viscosities, preferably from about 1 cS to about 200,000 cS, at 25 °C.

Additional Components

A wide variety of additional components can be employed in the topical personal care compositions herein. Non-limiting examples include the following.

Pharmaceutical Actives

5 The compositions of the present invention can comprise a safe and effective amount of a pharmaceutical active. The phrase "safe and effective amount", as used herein, means an amount of an active high enough to significantly or positively modify the condition to be treated, but low enough to avoid serious side effects (at a reasonable benefit/risk ratio), within the scope of sound medical judgement. A safe and effective amount of the pharmaceutical active will vary with the specific active,
10 the ability of the composition to penetrate the active through the skin, the amount of composition to be applied, the particular condition being treated, the age and physical condition of the patient being treated, the severity of the condition, the duration of the treatment, the nature of concurrent therapy, and like factors.

The pharmaceutical actives which can be used in the compositions of the present invention preferably comprise from about 0.1% to about 20% by weight of the compositions, more preferably from about 0.1% to about 10%, and most preferably from about 0.1% to about 5%. Mixtures of pharmaceutical actives may also be used.

Nonlimiting examples of pharmaceutical actives can include the following:

20 Useful pharmaceutical actives in the compositions of the present invention include anti-acne drugs. Anti-acne drugs preferred for use in the present invention include the keratolytics such as salicylic acid, sulfur, lactic acid, glycolic, pyruvic acid, urea, resorcinol, and N-acetylcysteine; retinoids such as retinoic acid and its derivatives (e.g., cis and trans); antibiotics and antimicrobials such as benzoyl peroxide, octopirox, erythromycin, zinc, tetracyclin, triclosan, azelaic acid and its
25 derivatives, phenoxy ethanol and phenoxy propanol, ethylacetate, clindamycin and meclocycline; sebostats such as flavinoids; alpha and beta hydroxy acids; and bile salts such as scymnol sulfate and its derivatives, deoxycholate, and cholate. Preferred for use herein is salicylic acid.

30 Useful pharmaceutical actives in the compositions of the present invention include non-steroidal anti-inflammatory drugs (NSAIDS). The NSAIDS can be selected from the following categories: propionic acid derivatives; acetic acid derivatives; fenamic acid derivatives; biphenylcarboxylic acid derivatives; and oxicams. All of these NSAIDS are fully described in the U.S. Patent 4,985,459 to
35 Sunshine et al., issued January 15, 1991, incorporated by reference herein. Most preferred are the propionic NSAIDS including but not limited to aspirin, acetaminophen, ibuprofen, naproxen, benoxaprofen, flurbiprofen, fenoprofen,

fenbufen, ketoprofen, indoprofen, piroprofen, carprofen, oxaprozin, pranoprofen, miroprofen, tioxaprofen, suprofen, alminoprofen, tiaprofenic acid, fluprofen and bucloxic acid. Also useful are the steroidal anti-inflammatory drugs including hydrocortisone and the like.

- 5 Useful pharmaceutical actives in the compositions of the present invention include antipruritic drugs. Antipruritic drugs preferred for inclusion in compositions of the present invention include pharmaceutically-acceptable salts of methdilazine and trimeprazine. Useful pharmaceutical actives in the compositions of the present invention include anesthetic drugs. Anesthetic drugs preferred for inclusion
- 10 in compositions of the present invention include pharmaceutically-acceptable salts of lidocaine, bupivacaine, chlorprocaine, dibucaine, etidocaine, mepivacaine, tetracaine, dyclonine, hexylcaine, procaine, cocaine, ketamine, pramoxine and phenol. Useful pharmaceutical actives in the compositions of the present invention include antimicrobial drugs (antibacterial, antifungal, antiprotozoal and antiviral drugs).
- 15 Antimicrobial drugs preferred for inclusion in compositions of the present invention include pharmaceutically-acceptable salts of b-lactam drugs, quinolone drugs, ciprofloxacin, norfloxacin, tetracycline, erythromycin, amikacin, triclosan, doxycycline, capreomycin, chlorhexidine, chlortetracycline, oxytetracycline, clindamycin, ethambutol, metronidazole, pentamidine, gentamicin, kanamycin,
- 20 lineomycin, methacycline, methenamine, minocycline, neomycin, netilmicin, paromomycin, streptomycin, tobramycin, miconazole and amantadine. Antimicrobial drugs preferred for inclusion in compositions of the present invention include tetracycline hydrochloride, erythromycin estolate, erythromycin stearate (salt), amikacin sulfate, doxycycline hydrochloride, capreomycin sulfate, chlorhexidine
- 25 gluconate, chlorhexidine hydrochloride, chlortetracycline hydrochloride, oxytetracycline hydrochloride, clindamycin hydrochloride, ethambutol hydrochloride, metronidazole hydrochloride, pentamidine hydrochloride, gentamicin sulfate, kanamycin sulfate, lineomycin hydrochloride, methacycline hydrochloride, methenamine hippurate, methenamine mandelate, minocycline hydrochloride,
- 30 neomycin sulfate, netilmicin sulfate, paromomycin sulfate, streptomycin sulfate, tobramycin sulfate, miconazole hydrochloride, amantadine hydrochloride, amantadine sulfate, triclosan, octopirox, parachlorometa xyleneol, nystatin, tolnaftate and clotrimazole.

- 35 A wide variety of alpha-hydroxy acids and beta-hydroxy acids can be useful for pharmaceutical and cosmetic purposes for the skin, including for anti-aging, reduced dryness, skin exfoliation, and reduction in the appearance of wrinkles and fine lines. These include salicylic acid, glycolic acid, and lactic acid.

Also useful herein are sunscreen agents. A wide variety of sunscreens are described in U.S. Patent No. 5,087,445, to Haffey et al., issued February 11, 1992; U.S. Patent No. 5,073,372, to Turner et al., issued December 17, 1991; U.S. Patent No. 5,073,371, to Turner et al. issued December 17, 1991; and Segarin, et al., at Chapter VIII, pages 189 et seq., of Cosmetics Science and Technology, all of which are incorporated herein by reference in their entirety. Included among those sunscreens are those selected from the group consisting of 2-ethylhexyl p-methoxycinnamate, 2-ethylhexyl N,N-dimethyl-p-aminobenzoate, p-aminobenzoic acid, 2-phenylbenzimidazole-5-sulfonic acid, octocrylene, oxybenzone, homomenthyl salicylate, octyl salicylate, 4,4'-methoxy-t-butylidibenzoylmethane, 4-isopropyl dibenzoylmethane, 3-benzylidene camphor, 3-(4-methylbenzylidene) camphor, titanium dioxide, zinc oxide, silica, iron oxide, and mixtures thereof.

Generally, the sunscreens can comprise from about 0.5% to about 20% of the compositions useful herein. Exact amounts will vary depending upon the sunscreen chosen and the desired Sun Protection Factor (SPF). SPF is a commonly used measure of photoprotection of a sunscreen against erythema. See Federal Register, Vol. 43, No. 166, pp. 38206-38269, August 25, 1978, which is incorporated herein by reference in its entirety.

Also useful in the present invention are sunless tanning agents including dihydroxyacetone, glyceraldehyde, indoles and their derivatives, and the like. These sunless tanning agents may also be used in combination with the sunscreen agents.

Other useful actives include skin bleaching (or lightening) agents including but not limited to hydroquinone, ascorbic acid, kojic acid and sodium metabisulfite.

Other useful actives which are especially useful for hair care compositions include anti-dandruff actives such as zinc pyrithione, octopirox, selenium disulfide, sulfur, coal tar, and the like.

Zinc pyrithione and triclosan, as well as other anti-bacterials, may also be used in anti-perspirant compositions and deodorant compositions for use on the body, especially in the underarm area.

Conditioners

The compositions of the present invention can comprise a wide variety of conditioning agents for the hair or skin. The conditioning agents are typically used at a level of from about 0.05% to about 20%, by weight of the composition, preferably from about 0.1% to about 10%, more preferably from about 0.5% to about 5%. Nonvolatile, as used herein, has the meaning as defined above.

Conditioning agents useful herein, and especially useful for hair care and skin care compositions, include nonvolatile conditioning fluids, such as hydrocarbons, silicone fluids, fatty esters, and fatty alcohols, as well as cationic materials.

5 The conditioning fluids will generally have a viscosity of about 3 million cs or less, preferably about 2 million cs or less, more preferably about 1.5 million cs or less.

10 Conditioning fluids include liquids selected from the group consisting of hydrocarbon oils and fatty esters. The fatty esters include compounds characterized by having at least 10 carbon atoms, and include esters with hydrocarbyl chains derived from fatty acids or alcohols, e.g., mono-esters, polyhydric alcohol esters, and di- and tri-carboxylic acid esters. The hydrocarbyl radicals of the fatty esters hereof can also include or have covalently bonded thereto other compatible functionalities, such as amides and alkoxy moieties (e.g., ethoxy or ether linkages, etc.).

15 Hydrocarbon oils include cyclic hydrocarbons, straight chain aliphatic hydrocarbons (saturated or unsaturated), and branched chain aliphatic hydrocarbons (saturated or unsaturated). Straight chain hydrocarbon oils will preferably contain from about 12 to about 19 carbon atoms, although it is not necessarily meant to be limit the hydrocarbons to this range. Branched chain hydrocarbon oils can and typically may contain higher numbers of carbon atoms. Also encompassed herein are 20 polymeric hydrocarbons of alkenyl monomers, such as C_2-C_6 alkenyl monomers. Specific examples of suitable materials include paraffin oil, mineral oil, saturated and unsaturated dodecane, saturated and unsaturated tridecane, saturated and unsaturated tetradecane, saturated and unsaturated pentadecane, saturated and unsaturated hexadecane, and mixtures thereof. A preferred hydrocarbon polymer is polybutene, 25 such as the copolymer of isobutylene and butene. A commercially available material of this type is L-14 polybutene from Amoco Chemical Co. (Chicago, Illinois, U.S.A.).

30 Monocarboxylic acid esters hereof include esters of alcohols and/or acids of the formula $R'COOR$ wherein alkyl or alkenyl radicals and the sum of carbon atoms in R' and R is at least 10, preferably at least 20.

Fatty esters include, for example, alkyl and alkenyl esters of fatty acids having aliphatic chains with from about 10 to about 22 carbon atoms, and alkyl and alkenyl fatty alcohol carboxylic acid esters having an alkyl and/or alkenyl alcohol-derived aliphatic chain with about 10 to about 22 carbon atoms, and combinations thereof. 35 Examples include isopropyl isostearate, hexyl laurate, isohexyl laurate, isohexyl palmitate, isopropyl palmitate, decyl oleate, isodecyl oleate, hexadecyl stearate, decyl stearate, isopropyl isostearate, dihexyldecyl adipate, lauryl lactate, myristyl lactate,

cetyl lactate, oleyl stearate, oleyl oleate, oleyl myristate, lauryl acetate, cetyl propionate, and oleyl adipate. The mono-carboxylic acid ester however need not necessarily contain at least one chain with at least 10 carbon atoms, so long as the total number of aliphatic chain carbon atoms is at least 10. Examples include

5 diisopropyl adipate, diisohexyl adipate, and diisopropyl sebacate.

Di- and tri-alkyl and alkenyl esters of carboxylic acids can also be used. These include, for example, esters of C₄-C₈ dicarboxylic acids such as C₁-C₂₂ esters (preferably C₁-C₆) of succinic acid, glutaric acid, adipic acid, hexanoic acid, heptanoic acid, and octanoic acid. Specific examples include isocetyl stearyl

10 stearate, diisopropyl adipate, and tristearyl citrate.

Polyhydric alcohol esters include alkylene glycol esters, for example ethylene glycol mono and di-fatty acid esters, diethylene glycol mono- and di-fatty acid esters, polyethylene glycol mono- and di-fatty acid esters, propylene glycol mono- and di-fatty acid esters, polypropylene glycol monooleate, polypropylene glycol 2000

15 monostearate, ethoxylated propylene glycol monostearate, glyceryl mono- and di-fatty acid esters, polyglycerol poly-fatty acid esters, ethoxylated glyceryl monostearate, 1,3-butylene glycol monostearate, 1,3-butylene glycol distearate, polyoxyethylene polyol fatty acid ester, sorbitan fatty acid esters, and polyoxyethylene sorbitan fatty acid esters are satisfactory polyhydric alcohol esters for use

20 herein.

Glycerides include mono-, di-, and tri-glycerides. More specifically, included are the mono-, di-, and tri-esters of glycerol and long chain carboxylic acids, such as C₁₀-C₂₂ carboxylic acids. A variety of these types of materials can be obtained from vegetable and animal fats and oils, such as castor oil, safflower oil, cottonseed oil,

25 corn oil, olive oil, cod liver oil, almond oil, avocado oil, palm oil, sesame oil, lanolin and soybean oil. Synthetic oils include triolein and tristearin glyceryl dilaurate. Preferred glycerides are di-, and tri-glycerides. Especially preferred are triglycerides.

Other conditioning agents fluids include fatty alcohols, preferably C₁₀-C₂₂ alcohols, such as stearyl and cetyl alcohols.

30 Still other conditioning agents for hair and/or skin include urea; guanidine; aloe vera in any of its variety of forms (e.g., aloe vera gel); polyhydroxy alcohols such as sorbitol, glycerol, hexanetriol, propylene glycol, butylene glycol, hexylene glycol and the like; polyethylene glycols; sugars and starches; sugar and starch derivatives (e.g., alkoxylated glucose); hyaluronic acid; lactamide monoethanolamine; acetamide

35 monoethanolamine; and mixtures thereof.

Silicone Conditioning Agent

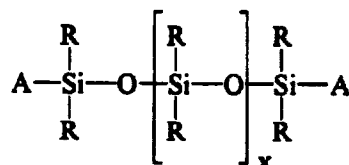
An optional component of the present invention is a nonvolatile, silicone conditioning agent.

The silicone conditioning agent for use herein will preferably have an average viscosity of from about 1,000 to about 2,000,000 centistokes at 25°C, more preferably from about 10,000 to about 1,800,000, even more preferably from about 100,000 to about 1,500,000. The viscosity of silicones herein can, in general, be measured by means of a glass capillary viscometer as set forth in Dow Corning Corporate Test Method CTM0004, July 20, 1970.

The silicone conditioning agent will typically be used in the compositions hereof at levels of from about 0.05% to about 10% by weight of the composition, preferably from about 0.1% to about 10%, more preferably from about 0.5% to about 8%, most preferably from about 0.5% to about 5%.

Suitable insoluble, nonvolatile silicone conditioning agents include polyalkyl siloxanes, polyaryl siloxanes, polyalkylaryl siloxanes, polyether siloxane copolymers, and mixtures thereof. Other insoluble, nonvolatile silicones can also be used. The silicones hereof can be silicone fluids or silicone gums. The term "silicone fluid" shall mean flowable silicone materials having a viscosity of less than 1,000,000 centistokes at 25°C. Generally, the viscosity of the fluid will be between about 5 and 1,000,000 centistokes at 25°C, preferably between about 10 and about 100,000. Silicone gums are described in more detail below.

Silicone fluids hereof include polyalkyl or polyaryl siloxanes with the following structure:



wherein R is alkyl or aryl, and x is an integer from about 1 to about 8,000, preferably from about 5 to about 8,000. "A" represents groups which block the ends of the silicone chains.

The alkyl or aryl groups substituted on the siloxane chain (R) or at the ends of the siloxane chains (A) may have any structure as long as the resulting silicones remain fluid at room temperature, are hydrophobic, are neither irritating, toxic nor otherwise harmful when applied to the hair, are compatible with the other components of the composition, are chemically stable under normal use and storage conditions, and are capable of being deposited on and of conditioning hair.

Suitable A groups include methyl, methoxy, ethoxy, propoxy, and aryloxy. The two R groups on the silicone atom may represent the same group or different groups. Preferably, the two R groups represent the same group. Suitable R groups include methyl, ethyl, propyl, phenyl, methylphenyl and phenylmethyl. The preferred
5 silicones are polydimethyl siloxane, polydiethylsiloxane, and polymethylphenylsiloxane. Polydimethylsiloxane is especially preferred.

The nonvolatile polyalkylsiloxane fluids that may be used include, for example, polydimethylsiloxanes. These siloxanes are available, for example, from the General Electric Company in their Viscasil^R and SF 96 series, and from Dow
10 Corning in their Dow Corning 200 series.

The polyalkylaryl siloxane fluids that may be used, also include, for example, polymethylphenylsiloxanes. These siloxanes are available, for example, from the General Electric Company as SF 1075 methyl phenyl fluid or from Dow Corning as 556 Cosmetic Grade Fluid.

15 The polyether siloxane copolymers that may be used include, for example, a polypropylene oxide modified polydimethylsiloxane (e.g., Dow Corning DC-1248) although ethylene oxide or mixtures of ethylene oxide and propylene oxide may also be used. The ethylene oxide and polypropylene oxide level must be sufficiently low to prevent solubility in water and the composition hereof.

20 Another silicone material that can be especially useful in the silicone conditioning agents is insoluble silicone gum. The term "silicone gum", as used herein, means polyorganosiloxane materials having a viscosity at 25°C of greater than or equal to 1,000,000 centistokes. Silicone gums are described by Petrarch and others including U.S. Patent 4,152,416, Spitzer et al., issued May 1, 1979 and Noll,
25 Walter, Chemistry and Technology of Silicones, New York: Academic Press 1968. Also describing silicone gums are General Electric Silicone Rubber Product Data Sheets SE 30, SE 33, SE 54 and SE 76. All of these described references are incorporated herein by reference. The "silicone gums" will typically have a mass molecular weight in excess of about 200,000, generally between about 200,000 and
30 about 1,000,000. Specific examples include polydimethylsiloxane, (polydimethylsiloxane) (methylvinylsiloxane) copolymer, poly(dimethylsiloxane) (diphenyl siloxane)(methylvinylsiloxane) copolymer and mixtures thereof.

Cationic Polymer Hair Conditioning Agent

35 The compositions of the present invention can also comprise cationic polymer conditioning agents. The polymeric cationic conditioning agents hereof will generally be used at levels of from about 0.05% to about 5%, preferably from about 0.1% to about 4%, more preferably from about 0.2% to about 3%, by weight, of the shampoo

composition. The cationic conditioning polymers are preferably water soluble. By "water soluble" cationic organic polymer, what is meant is a polymer which is sufficiently soluble in water to form a substantially clear solution to the naked eye at a concentration of 0.1% in water (distilled or equivalent) at 25°C. Preferably, the polymer will be sufficiently soluble to form a substantially clear solution at 0.5% concentration, more preferably at 1.0% concentration. The cationic polymers hereof will generally have a weight average molecular weight which is at least about 5,000, typically at least about 10,000, and up to about 10 million. Preferably, the molecular weight is from about 100,000 to about 2 million. The cationic polymers can generally be characterized by having have cationic nitrogen-containing moieties such as quaternary ammonium or cationic amino moieties, or a mixture thereof. Any anionic counterions can be utilized for the cationic polymers so long as the water solubility criteria is met. Suitable counterions include halides (e.g., Cl-, Br-, I-, or F-, preferably Cl-, Br-, or I-), sulfate, and methylsulfate. Others can also be used, as this list is not exclusive.

The cationic nitrogen-containing moiety will be present generally as a substituent, on a fraction of the total monomer units of the cationic hair conditioning polymers. Thus, the cationic polymer can comprise copolymers, terpolymers, etc. of quaternary ammonium or cationic amine-substituted monomer units and other non-cationic units referred to herein as spacer monomer units. Such polymers are known in the art, and a variety can be found in the CTFA Cosmetic Ingredient Dictionary, 3rd edition, edited by Estrin, Crosley, and Haynes, (The Cosmetic, Toiletry, and Fragrance Association, Inc., Washington, D.C., 1982).

Suitable cationic polymers include, for example, copolymers of vinyl monomers having cationic amine or quaternary ammonium functionalities with water soluble spacer monomers such as acrylamide, methacrylamide, alkyl and dialkyl acrylamides, alkyl and dialkyl methacrylamides, alkyl acrylate, alkyl methacrylate, vinyl caprolactone, and vinyl pyrrolidone. The alkyl and dialkyl substituted monomers preferably have C₁-C₇ alkyl groups, more preferably C₁-C₃ alkyl groups. Other suitable spacer monomers include vinyl esters, vinyl alcohol (made by hydrolysis of polyvinyl acetate), maleic anhydride, propylene glycol, and ethylene glycol.

The cationic amines can be primary, secondary, or tertiary amines, depending upon the particular species and the pH of the shampoo. In general, secondary and tertiary amines, especially tertiary amines, are preferred.

Amine-substituted vinyl monomers can be polymerized in the amine form, and then optionally can be converted to ammonium by a quaternization reaction. Amines

can also be similarly quaternized subsequent to formation of the polymer. For example, tertiary amine functionalities can be quaternized by reaction with a salt of the formula R'X wherein R' is a short chain alkyl, preferably a C₁-C₇ alkyl, more preferably a C₁-C₃ alkyl, and X is an anion which forms a water soluble salt with the quaternized ammonium.

Suitable cationic amino and quaternary ammonium monomers include, for example, vinyl compounds substituted with dialkylaminoalkyl acrylate, dialkylaminoalkyl methacrylate, monoalkylaminoalkyl acrylate, monoalkylaminoalkyl methacrylate, trialkyl methacryloxyalkyl ammonium salt, trialkyl acryloxyalkyl ammonium salt, diallyl quaternary ammonium salts, and vinyl quaternary ammonium monomers having cyclic cationic nitrogen-containing rings such as pyridinium, imidazolium, and quaternized pyrrolidone, e.g., alkyl vinyl imidazolium, alkyl vinyl pyridinium, alkyl vinyl pyrrolidone salts. The alkyl portions of these monomers are preferably lower alkyls such as the C₁-C₃ alkyls, more preferably C₁ and C₂ alkyls.

Suitable amine-substituted vinyl monomers for use herein include dialkylaminoalkyl acrylate, dialkylaminoalkyl methacrylate, dialkylaminoalkyl acrylamide, and dialkylaminoalkyl methacrylamide, wherein the alkyl groups are preferably C₁-C₇ hydrocarbyls, more preferably C₁-C₃, alkyls.

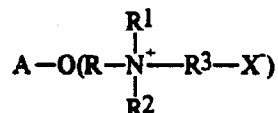
The cationic polymers hereof can comprise mixtures of monomer units derived from amine- and/or quaternary ammonium-substituted monomer and/or compatible spacer monomers.

Suitable cationic hair conditioning polymers include, for example: copolymers of 1-vinyl-2-pyrrolidone and 1-vinyl-3-methylimidazolium salt (e.g., chloride salt) (referred to in the industry by the Cosmetic, Toiletry, and Fragrance Association, "CTFA", as Polyquaternium-16), such as those commercially available from BASF Wyandotte Corp. (Parsippany, NJ, USA) under the LUVIQUAT tradename (e.g., LUVIQUAT FC 370); copolymers of 1-vinyl-2-pyrrolidone and dimethylaminoethyl methacrylate (referred to in the industry by CTFA as Polyquaternium-11) such as those commercially available from Gaf Corporation (Wayne, NJ, USA) under the GAFQUAT tradename (e.g., GAFQUAT 755N); cationic diallyl quaternary ammonium-containing polymers, including, for example, dimethyldiallylammonium chloride homopolymer and copolymers of acrylamide and dimethyldiallylammonium chloride, referred to in the industry (CTFA) as Polyquaternium 6 and Polyquaternium 7, respectively; and mineral acid salts of amino-alkyl esters of homo- and co-polymers of unsaturated carboxylic acids having from 3 to 5 carbon atoms, as described in U.S. Patent 4,009,256, incorporated herein by reference.

Other cationic polymers that can be used include polysaccharide polymers, such as cationic cellulose derivatives and cationic starch derivatives.

Cationic polysaccharide polymer materials suitable for use herein include those of the formula:

5



wherein: A is an anhydroglucose residual group, such as a starch or cellulose anhydroglucose residual,

R is an alkylene oxyalkylene, polyoxyalkylene, or hydroxyalkylene group, or
10 combination thereof,

R¹, R², and R³ independently are alkyl, aryl, alkylaryl, arylalkyl, alkoxyalkyl, or alkoxyaryl groups, each group containing up to about 18 carbon atoms, and the total number of carbon atoms for each cationic moiety (i.e., the sum of carbon atoms in R¹, R² and R³) preferably being about 20 or less, and

15 X is an anionic counterion, as previously described.

Cationic cellulose is available from Amerchol Corp. (Edison, NJ, USA) in their Polymer JR^R and LR^R series of polymers, as salts of hydroxyethyl cellulose reacted with trimethyl ammonium substituted epoxide, referred to in the industry (CTFA) as Polyquaternium 10. Another type of cationic cellulose includes the poly-
20 meric quaternary ammonium salts of hydroxyethyl cellulose reacted with lauryl dimethyl ammonium-substituted opoxide, referred to in the industry (CTFA) as Polyquaternium 24. These materials are available from Amerchol Corp. (Edison, NJ, USA) under the tradename Polymer LM-200.

Other cationic polymers that can be used include cationic guar gum
25 derivatives, such as guar hydroxypropyltrimonium chloride (commercially available from Celanese Corp. in their Jaguar^R series). Other materials include quaternary nitrogen-containing cellulose ethers (e.g., as described in U.S. Patent 3,962,418, incorporated by reference herein), and copolymers of etherified cellulose and starch (e.g., as described in U.S. Patent 3,958,581, incorporated by reference herein).

30 Cationic Surfactant Conditioning Agent

Cationic surfactants useful herein as conditioning agents include quaternary ammonium salts or the salts of fatty amines. Preferred quaternary ammonium salts are dialkyl dimethyl ammonium chlorides, wherein the alkyl groups have from 12 to 22 carbon atoms and are derived from long-chain fatty acids. Representative
35 examples of quaternary ammonium salts include ditallow dimethyl ammonium

chloride, ditallow dimethyl ammonium methyl sulfate, dihexadecyl dimethyl ammonium chloride, and di(hydrogenated tallow) ammonium chloride. Other quaternary ammonium salts useful herein are dicationics such as tallow propane diammonium dichloride. Quaternary imidazolinium salts are also useful herein.

5 Examples of such materials are those imidazolinium salts containing C12-22 alkyl groups such as 1-methyl-1-[(stearoylamide)ethyl]-2-heptadecyl-4, 5-dihydroimidazolinium chloride, 1-methyl-1-[(palmitoylamide)ethyl]-2-octadecyl-4, 5-dihydroimidazolinium chloride and 1-methyl-1-[(tallowamide)-ethyl]-2-tallow-imidazolinium methyl sulfate. Also useful herein are salts of fatty amines. Examples

10 of such compounds include stearylamine hydrochloride, soyamine hydrochloride, and stearylamine formate. Useful conditioning agents are disclosed in U.S. Patent No. 4,387,090, to Bolich, issued June 7, 1983, which is incorporated by reference herein.

Cationic surfactant conditioning agents are generally used at a level of from about 0.1% to about 5%, by weight of the composition.

15 Surfactants

Surfactants are optional ingredients in the compositions of the invention. When present, the surfactant typically comprises from about 0.05% to about 50% of the composition. Surfactants are especially useful in cleansing compositions, such as shampoos and skin cleansing compositions, and can be used for a wide variety of

20 other purposes in these and other types of compositions hereof. Exemplary uses include emulsifiers, solublizers of other ingredients, and conditioning (particularly cationic surfactants. For a shampoo or other cleansing composition, the surfactant level is preferably from about 5% to about 30%, more preferably from 12% to about 25%, of the composition. For conditioners, the preferred level of surfactant is from

25 about 0.05% to about 5%. Surfactants useful in compositions of the present invention include anionic, nonionic, cationic, and amphoteric surfactants. A wide variety of surfactants useful herein are disclosed in U.S. Patent No. 5,151,209, to Mc Call et al., issued September 29, 1992; U.S. Patent No. 5,151,210, to Steuri et al., issued September 29, 1992; and U.S. Patent No. 5,120,532, to Wells et al., issued

30 June 9, 1992, all of which are incorporated by reference herein.

Anionic detergents useful herein include alkyl and alkyl ether sulfates. These materials typically have the respective formulae ROSO_3M and $\text{RO}(\text{C}_2\text{H}_4\text{O})_x\text{SO}_3\text{M}$, wherein R is alkyl or alkenyl of from about 10 to about 20 carbon atoms, x is 1 to 10, and M is a water-soluble cation such as ammonium, sodium, potassium and

35 triethanolamine.

Another suitable class of anionic surfactants are the water-soluble salts of the organic, sulfuric acid reaction products of the general formula:

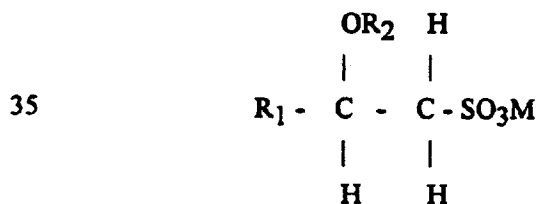


wherein R_1 is chosen from the group consisting of a straight or branched chain, saturated aliphatic hydrocarbon radical having from about 8 to about 24, preferably about 12 to about 18, carbon atoms; and M is a cation. Important examples are the salts of an organic sulfuric acid reaction product of a hydrocarbon of the methane series, including iso-, neo-, and n-paraffins, having about 8 to about 24 carbon atoms, preferably about 12 to about 18 carbon atoms and a sulfonating agent, e.g., SO_3 , H_2SO_4 , oleum, obtained according to known sulfonation methods, including bleaching and hydrolysis. Preferred are alkali metal and ammonium sulfonated C_{12} -18 n-paraffins.

Additional examples of anionic synthetic surfactants which come within the terms of the present invention are the reaction products of fatty acids esterified with isethionic acid and neutralized with sodium hydroxide where, for example, the fatty acids are derived from coconut oil; sodium or potassium salts of fatty acid amides of methyl tauride in which the fatty acids, for example, are derived from coconut oil. Other anionic synthetic surfactants of this variety are set forth in U.S. Patents 2,486,921; 2,486,922; and 2,396,278.

Still other anionic synthetic surfactants include the class designated as succinamates. This class includes such surface active agents as disodium N-octadecylsulfosuccinamate; tetrasodium N-(1,2-dicarboxyethyl)-N-octadecylsulfosuccinamate; diamyl ester of sodium sulfosuccinic acid; dihexyl ester of sodium sulfosuccinic acid; dioctyl esters of sodium sulfosuccinic acid.

Other suitable anionic surfactants utilizable herein are olefin sulfonates having about 12 to about 24 carbon atoms. The term "olefin sulfonates" is used herein to mean compounds which can be produced by the sulfonation of α -olefins by means of uncomplexed sulfur trioxide, followed by neutralization of the acid reaction mixture in conditions such that any sultones which have been formed in the reaction are hydrolyzed to give the corresponding hydroxy-alkanesulfonates. The α -olefins from which the olefin sulfonates are derived are mono-olefins having about 12 to about 24 carbon atoms, preferably about 14 to about 16 carbon atoms. Another class of anionic organic surfactants are the β -alkyloxy alkane sulfonates. These compounds have the following formula:



where R_1 is a straight chain alkyl group having from about 6 to about 20 carbon atoms, R_2 is a lower alkyl group having from about 1 (preferred) to about 3 carbon atoms, and M is a water-soluble cation as hereinbefore described.

Many additional nonsoap synthetic anionic surfactants are described in
 5 McCutcheon's, Detergents and Emulsifiers, 1984 Annual, published by Allured Publishing Corporation, which is incorporated herein by reference. Also U.S. Patent 3,929,678, Laughlin et al., issued December 30, 1975, discloses many other anionic as well as other surfactant types and is incorporated herein by reference. Soaps can also be utilized as anionic surfactants.

10 Nonionic surfactants, can be broadly defined as compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. Examples of classes of nonionic surfactants are:

1. Those derived from the condensation of ethylene oxide with the
 15 product resulting from the reaction of propylene oxide and ethylene diamine products.

2. The condensation product of aliphatic alcohols having from about 8 to about 18 carbon atoms, in either straight chain or branched chain configuration, with ethylene oxide, e.g., a coconut alcohol ethylene oxide condensate having from about
 20 10 to about 30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from about 10 to about 14 carbon atoms.

3. Long chain tertiary amine oxides such as those corresponding to the following general formula:



25 wherein R_1 contains an alkyl, alkenyl or monohydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties, and from 0 to about 1 glyceryl moiety, and R_2 and R_3 contain from about 1 to about 3 carbon atoms and from 0 to about 1 hydroxy group, e.g., methyl, ethyl, propyl, hydroxyethyl, or hydroxypropyl radicals (the arrow in the formula is a conventional
 30 representation of a semipolar bond).

4. Long chain tertiary phosphine oxides corresponding to the following general formula:



wherein R contains an alkyl, alkenyl or monohydroxyalkyl radical ranging from about
 35 8 to about 18 carbon atoms in chain length, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety and R' and R'' are each alkyl or

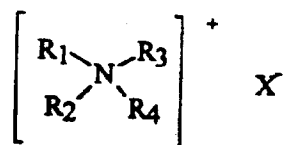
monohydroxyalkyl groups containing from about 1 to about 3 carbon atoms. The arrow in the formula is a conventional representation of a semipolar bond.

- 5 Long chain dialkyl sulfoxides containing one short chain alkyl or hydroxy alkyl radical of from about 1 to about 3 carbon atoms (usually methyl) and one long hydrophobic chain which include alkyl, alkenyl, hydroxy alkyl, or keto alkyl radicals containing from about 8 to about 20 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety. Examples include: octadecyl methyl sulfoxide, 2-ketotridecyl methyl sulfoxide, 3,6,9-triaoctadecyl 2-hydroxyethyl sulfoxide, dodecyl methyl sulfoxide, oleyl 3-hydroxypropyl sulfoxide, tetra decyl methyl sulfoxide, 3-methoxytridecyl methyl sulfoxide, 3-hydroxytridecyl methyl sulfoxide, 3-hydroxy-4-dodecoxybutyl methyl sulfoxide.

- 6 N-Polyhydroxy fatty acid amides, such as the polyhydroxyhydrocarbonyl C9-C19 fatty acid amides having polyhydroxy functionalities with at least three hydroxy groups, preferably derived from reducing sugars such as glucose, fructose, maltose, lactose, and the like. Surfactants of this type are disclosed in US Patent 2,965,576, E. R. Wilson, issued December 20, 1960, incorporated herein by reference.

- Cationic surfactants useful in compositions of the present invention, particularly the conditioner compositions, contain amino or quaternary ammonium hydrophilic moieties which are positively charged when dissolved in the aqueous composition of the present invention. Cationic surfactants among those useful herein are disclosed in the following documents, all incorporated by reference herein: M.C. Publishing Co., McCutcheon's Detergents & Emulsifiers, (North American edition 1979); Schwartz, et al., Surface Active Agents, Their Chemistry and Technology, New York: Interscience Publishers, 1949; U.S. Patent 3,155,591, Hilfer, issued November 3, 1964; U.S. Patent 3,929,678, Laughlin, et al., issued December 30, 1975; U.S. Patent 3,959,461, Bailey, et al., issued May 25, 1976; and U.S. Patent 4,387,090, Bolich, Jr., issued June 7, 1983. If included in the compositions of the present invention, the cationic surfactant is generally present at from about 0.05% to about 5%.

Among the quaternary ammonium-containing cationic surfactant materials useful herein are those of the general formula:



wherein R₁-R₄ are independently an aliphatic group of from about 1 to about 22 carbon atoms, or an aromatic, alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, aryl or alkylaryl group having from about 12 to about 22 carbon atoms; and X is an anion selected from halogen, acetate, phosphate, nitrate and alkylsulfate radicals. The aliphatic groups may contain, in addition to carbon and hydrogen atoms, ether linkages, and other groups such as amino groups. The longer chain aliphatic groups, e.g., those of about 12 carbons, or higher, can be saturated or unsaturated.

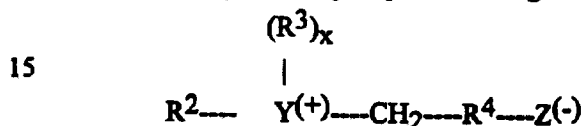
Other quaternary ammonium salts useful herein are diquaternary ammonium salts, such as tallow propane diammonium dichloride.

Quaternary ammonium salts include dialkyldimethyl-ammonium chlorides, wherein the alkyl groups have from about 12 to about 22 carbon atoms and are derived from long-chain fatty acids, such as hydrogenated tallow fatty acid (tallow fatty acids yield quaternary compounds wherein R₁ and R₂ have predominately from 16 to 18 carbon atoms). Examples of quaternary ammonium salts useful in the present invention include ditallowdimethyl ammonium chloride, ditallowdimethyl ammonium methyl sulfate, dihexadecyl dimethyl ammonium chloride, di(hydrogenated tallow) dimethyl ammonium chloride, dioctadecyl dimethyl ammonium chloride, diecosyl dimethyl ammonium chloride, didocosyl dimethyl ammonium chloride, di(hydrogenated tallow) dimethyl ammonium acetate, dihexadecyl dimethyl ammonium chloride, dihexadecyl dimethyl ammonium acetate, ditallow dipropyl ammonium phosphate, ditallow dimethyl ammonium nitrate, di(coconutalkyl) dimethyl ammonium chloride, and stearyl dimethyl benzyl ammonium chloride. Ditallow dimethyl ammonium chloride, dicetyl dimethyl ammonium chloride, stearyl dimethyl benzyl ammonium chloride and cetyl trimethyl ammonium chloride are preferred quaternary ammonium salts useful herein. Di-(saturated or unsaturated tallow) dimethyl ammonium chloride is a particularly preferred quaternary ammonium salt.

Salts of primary, secondary and tertiary fatty amines are also suitable cationic surfactant materials. The alkyl groups of such amines preferably have from about 12 to about 22 carbon atoms, and may be substituted or unsubstituted. Such amines, useful herein, include stearamido propyl dimethyl amine, diethyl amino ethyl stearamide, dimethyl stearamine, dimethyl soyamine, soyamine, myristyl amine, tridecyl amine, ethyl stearylamine, N-tallowpropane diamine, ethoxylated (5 moles

E.O.) stearylamine, dihydroxy ethyl stearylamine, and arachidylbehenylamine. Suitable amine salts include the halogen, acetate, phosphate, nitrate, citrate, lactate and alkyl sulfate salts. Such salts include stearylamine hydrochloride, soyamine chloride, stearylamine formate, N-tallowpropane diamine dichloride and
 5 stearamidopropyl dimethylamine citrate. Cationic amine surfactants included among those useful in the present invention are disclosed in U.S. Patent 4,275,055, Nachtigal, et al., issued June 23, 1981, incorporated by reference herein.

Amphoteric surfactants, include those which can be broadly described as derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium
 10 compounds, in which the aliphatic radicals can be straight or branched chain, and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water-solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. A general formula for these compounds is:



wherein R^2 contains an alkyl, alkenyl, or hydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety; Y is selected from the group consisting of nitrogen, phosphorus, and sulfur atoms; R^3 is an alkyl or monohydroxyalkyl group containing
 20 about 1 to about 3 carbon atoms; X is 1 when Y is a sulfur atom, and 2 when Y is a nitrogen or phosphorus atom; R^4 is an alkylene or hydroxyalkylene of from about 1 to about 4 carbon atoms and Z is a radical selected from the group consisting of carboxylate, sulfonate, sulfate, phosphonate, and phosphate groups.

Other amphoterics such as betaines are also useful in the present invention. Examples of betaines useful herein include the high alkyl betaines, such as coco dimethyl carboxymethyl betaine, lauryl dimethyl carboxymethyl betaine, lauryl dimethyl alpha carboxyethyl betaine, cetyl dimethyl carboxymethyl betaine, lauryl bis-(2-hydroxyethyl) carboxymethyl betaine, stearyl bis-(2-hydroxypropyl)
 30 carboxymethyl betaine, oleyl dimethyl gamma-carboxypropyl betaine, and lauryl bis-(2-hydroxypropyl)alpha-carboxyethyl betaine. The sulfobetaines may be represented by coco dimethyl sulfopropyl betaine, stearyl dimethyl sulfopropyl betaine, lauryl dimethyl sulfoethyl betaine, lauryl bis-(2-hydroxyethyl) sulfopropyl betaine and the like; amidobetaines and amidosulfobetaines, wherein the $RCONH(CH_2)_3$ radical is
 35 attached to the nitrogen atom of the betaine are also useful in this invention.

Other examples of amphoteric surfactants which can be used in the compositions of the present invention are those which are broadly described as

derivatives of aliphatic secondary and tertiary amines in which the aliphatic radical can be straight or branched chain and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate.

- 5 Examples of compounds falling within this definition are sodium 3-dodecylaminopropionate, sodium 3-dodecylamino propane sulfonate, N-alkyltaurines such as the one prepared by reacting dodecylamine with sodium isethionate according to the teaching of U.S. Patent 2,658,072, N-higher alkyl aspartic acids such as those produced according to the teaching of U.S. Patent 2,438,091, and the products sold
10 under the trade name "Miranol" and described in U.S. Patent 2,528,378.

Thickening and Suspending Agents

The compositions of the present invention can comprise a wide variety of rheological modifiers as thickening an/or suspending agents. Exemplary ingredients of this type are described below.

- 15 The compositions may include gel vehicle materials. These are particularly useful for use in products such as hair rinses, creams and lotions.

Gel vehicles can comprise two essential components: a lipid vehicle material and a cationic surfactant vehicle material. Cationic surfactant materials are described in detail below. Gel vehicles are generally described in the following documents, all
20 incorporated by reference herein: Barry, "The Self Bodying Action of the Mixed Emulsifier Sodium Dodecyl Sulfate/Cetyl Alcohol", 28 J. of Colloid and Interface Science 82-91 (1968); Barry, et al., "The Self-Bodying Action of Alkyltrimethylammonium Bromides/Cetostearyl Alcohol Mixed Emulsifiers, Influence of Quaternary Chain Length", 35 J. of Colloid and Interface Science 689-
25 708 (1971); and Barry, et al., "Rheology of Systems Containing Cetomacrogol 1000 - Cetostearyl Alcohol, I. Self Bodying Action", 38 J. of Colloid and Interface Science 616-625 (1972).

- The carrier may incorporate one or more lipid vehicle materials, regardless of whether it also contains a cationic surfactant, which are essentially water-insoluble,
30 and contain hydrophobic and hydrophilic moieties. Lipid vehicle materials include naturally or synthetically-derived acids, acid derivatives, alcohols, esters, ethers, ketones, and amides with carbon chains of from about 12 to about 22, preferably from about 16 to about 18, carbon atoms in length. Fatty alcohols and fatty esters are preferred; fatty alcohols are particularly preferred.

- 35 Preferred esters for use herein include cetyl palmitate and glycerylmonostearate. Cetyl alcohol and stearyl alcohol are preferred alcohols. A particularly preferred lipid vehicle material is comprised of a mixture of cetyl alcohol

and stearyl alcohol containing from about 55% to about 65% (by weight of mixture) of cetyl alcohol.

If included in the compositions of the present invention, the lipid vehicle material is typically present at from about 0.1% to about 10.0% of the composition; the cationic
5 surfactant vehicle material is present at from about 0.05% to about 5.0% of the composition.

The use of nonionic cellulose ethers and water-soluble gums for thickening compositions are also contemplated. See for example, U.S. Patent 4,557,928, Glover, issued December 10, 1985, teaching a hair conditioner comprising a
10 suspension system which consists of one of glucan gum, guar gum, and hydroxyethylcellulose; and U.S. Patent 4,581,230, Grollier et al., issued April 8, 1986, which teaches cosmetic compositions for treating hair which comprise as thickening agents hydroxyethylcellulose, or water-soluble vegetable thickening agents, such as guar gum, each incorporated herein by reference.

15 Cellulose ethers useful for producing viscous compositions include those having a sufficient degree of nonionic substituents selected from the group consisting of methyl, hydroxyethyl, and hydroxypropyl to cause them to be water-soluble and which are further substituted with a hydrocarbon radical having from about 10 to 24 carbon atoms in an amount between about 0.2 weight percent and the amount which
20 renders said cellulose ether less than 1%, by weight, soluble in water. The cellulose ether to be modified is preferably one of low to medium molecular weight; i.e., less than about 800,000 and preferably between about 20,000 and 700,000 (about 75 to 2500 D.P.).

Nonionic water-soluble cellulose ethers are preferred polymers that can be
25 employed in hair care compositions. Widely used, commercially-available nonionic cellulose ethers include methyl cellulose, hydroxy propyl methyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose and ethyl hydroxyethyl cellulose.

Other thickening agents for use in the compositions of the present invention, especially for hair rinses, include combinations of hydrophobically-modified
30 polymeric materials with surfactants, such as quaternary ammonium compounds (such as ditallowdimethyl ammonium chloride). These vehicles are described in detail in the following patents: U.S. Patent 5,106,609, issued April 21, 1992 to Bolich et al., U.S. Patent 5,100,658, issued March 31, 1992 to Bolich et al., U.S. Patent 5,104,646, issued April 14, 1992 to Bolich et al, and U.S. Patent 5,100,657,
35 issued March 31, 1992 to Ansher-Jackson et al., each incorporated herein by reference. By "hydrophobically modified nonionic water-soluble polymer" is meant a nonionic water-soluble polymer which has been modified by the substitution with a

sufficient amount of hydrophobic groups to make the polymer less soluble in water. By "water-soluble" what is meant is the polymer or salt, thereof, constituting the polymer backbone of the thickener should be sufficiently soluble such that it forms a substantially clear solution when dissolved in water at a level of 1%, by weight of the solution, at 25°C. Hence, the polymer backbone of the primary thickener can be essentially any water-soluble polymer. The hydrophobic groups can be C₈ to C₂₂ alkyl, aryl alkyl, alkyl aryl groups and mixtures thereof. The degree of hydrophobic substitution on the polymer backbone should be from about 0.10% to about 1.0%, depending on the particular polymer backbone. More generally, the ratio of hydrophilic portion to hydrophobic portion of the polymer is from about 10:1 to about 1000:1.

Nonionic water-soluble cellulose ethers are preferred to be employed as the polymer substrate of these hydrophobically modified polymers. Thus, e.g., hydroxyethyl cellulose, hydroxypropyl cellulose, methyl cellulose, hydroxypropyl methyl cellulose, ethyl hydroxyethyl cellulose, and methyl hydroxyethyl cellulose can be used.

It is also contemplated to utilize a suspending agent to thicken the compositions and/or suspend the insoluble ingredients of the composition. Suitable suspending agents are long chain acyl derivatives, long chain amine oxides, and mixtures thereof, wherein such suspending agents are present in the shampoo compositions in crystalline form. A variety of such suspending agents are described in U.S. Patent Reissue 34,584, Grote et al., issued April 12, 1994. Especially preferred is ethylene glycol distearate.

Also included among the long chain acyl derivatives useful as suspending agents are the N,N-di(hydrogenated) C₈-C₂₂ (preferably C₁₂-C₂₂, more preferably C₁₆-C₁₈) amido benzoic acid, or soluble salt (e.g., K, Na salts) thereof particularly N,N-di(hydrogenated)tallow amido benzoic acid which is commercially marketed by Stepan Company (Northfield, Illinois, USA).

Another component useful in the compositions for thickening or for suspending insoluble ingredients herein is a crosslinked carboxylic polymeric thickener. These crosslinked polymers contain one or more monomers derived from acrylic acid, substituted acrylic acids, and salts and esters of these acrylic acids and the substituted acrylic acids, wherein the crosslinking agent contains two or more carbon-carbon double bonds and is derived from a polyhydric alcohol.

Examples of commercially available carboxylic acid polymers include the carbomers, which are homopolymers of acrylic acid crosslinked with allyl ethers of sucrose or pentaerythritol. The carbomers are available as the Carbopol® 900 series

from B.F. Goodrich. Examples of commercially available copolymers also include copolymers of C₁₀₋₃₀ alkyl acrylates with one or more monomers of acrylic acid, methacrylic acid, or one of their short chain (i.e. C₁₋₄ alcohol) esters, wherein the crosslinking agent is an allyl ether of sucrose or pentaerytritol. These copolymers are known as acrylates/C₁₀₋₃₀ alkyl acrylate crosspolymers and are commercially available as Carbopol® 1342, Pemulen TR-1, and Pemulen TR-2, from B.F. Goodrich.

When used, the compositions of the present invention will generally comprise from about 0.01% to about 2%, more preferably from about 0.05% to about 1% and most preferably from about 0.10% to about 0.75% of the carboxylic acid polymer thickeners.

Other thickeners include: low pH thickening agents such as polyacrylamide, available as Sepigel from Seppic Corporation; and crosslinked methyl quaternized dimethylaminomethacrylate, available as Salcare SC95 from Allied Colloids.

Emulsifiers

The compositions herein can contain various emulsifiers. These emulsifiers are useful for emulsifying the various carrier components of the compositions herein, and are not required for solubilizing or dispersing the copolymers of the present invention. Suitable emulsifiers can include any of a wide variety of nonionic, cationic, anionic, and zwitterionic surfactants as disclosed above and as disclosed in the general literature. See, for example, McCutcheon's, Detergents and Emulsifiers, North American Edition (1986), published by Allured Publishing Corporation; U.S. Patent No. 5,011,681 to Ciotti et al., issued April 30, 1991; U.S. Patent No. 4,421,769 to Dixon et al., issued December 20, 1983; and U.S. Patent No. 3,755,560 to Dickert et al., issued August 28, 1973.

Suitable emulsifiers also include esters of glycerin, esters of propylene glycol, fatty acid esters of polyethylene glycol, fatty acid esters of polypropylene glycol, esters of sorbitol, esters of sorbitan anhydrides, carboxylic acid copolymers, esters and ethers of glucose, ethoxylated ethers, ethoxylated alcohols, alkyl phosphates, polyoxyethylene fatty ether phosphates, fatty acid amides, acyl lactylates, soaps and mixtures thereof.

Suitable emulsifiers also include, but are not limited to, polyethylene glycol 20 sorbitan monolaurate (Polysorbate 20), polyethylene glycol 5 soya sterol, Steareth-20, Cetareth-20, PPG-2 methyl glucose ether distearate, Ceteth-10, Polysorbate 80, cetyl phosphate, potassium cetyl phosphate, diethanolamine cetyl phosphate, Polysorbate 60, glyceryl stearate, PEG-100 stearate, and mixtures thereof. The emulsifiers can be used individually or as a mixture of two or more and can comprise

from about 0.1% to about 10%, more preferably from about 1% to about 7%, and most preferably from about 1% to about 5% of the compositions of the present invention.

Additional Components

5 The compositions herein can contain a variety of other optional components suitable for rendering such compositions more cosmetically or aesthetically acceptable, to improve storage stability and efficacy, or to provide them with additional usage benefits. Such conventional optional ingredients are well-known to those skilled in the art, e.g., colors and dyes, perfumes, pearlescent aids, such as
10 ethylene glycol distearate; preservatives, such as benzyl alcohol, methyl paraben, propyl paraben and imidazolidinyl urea; thickeners and viscosity modifiers, such as a diethanolamide of a long chain fatty acid (e.g., PEG 3 lauric diethanolamide), cocomonooethanol amide, guar gum, methyl cellulose, starches and starch derivatives; fatty alcohols, such as cetearyl alcohol; sodium chloride; sodium sulfate; polyvinyl
15 alcohol; ethyl alcohol; pH adjusting agents, such as citric acid, sodium citrate, succinic acid, phosphoric acid, sodium hydroxide, sodium carbonate; salts, in general, such as potassium acetate and sodium chloride; coloring agents, such as any of the FD&C or D&C dyes; perfumes; sequestering agents, such as disodium ethylenediamine tetra-acetate; polymer plasticizing agents, such as glycerin, disobutyl
20 adipate, butyl stearate, and propylene glycol; vitamins and derivatives thereof (e.g., ascorbic acid, vitamin E, tocopheryl acetate, retinoic acid, retinol, retinoids, and the like; skin sensates, astringents, skin soothing agents, skin healing agents and the like, nonlimiting examples of these aesthetic components include panthenol and derivatives (e.g. ethyl panthenol), pantothenic acid and its derivatives, clove oil,
25 menthol, camphor, eucalyptus oil, eugenol, menthyl lactate, witch hazel distillate, allantoin, bisababol, dipotassium glycyrrhizinate and the like.); polymers for aiding the film-forming properties and substantivity of the composition (such as a copolymer of eicosene and vinyl pyrrolidone, an example of which is available from GAF Chemical Corporation as Ganex^R V-220); preservatives for maintaining the antimicrobial
30 integrity of the compositions; skin penetration aids such as DMSO, 1-dodecylazacycloheptan-2-one (available as Azone from the Upjohn Co.); and the like. Such optional ingredients generally are used individually at levels of from about 0.01% to about 10.0%, preferably from about 0.05% to about 5.0%, of the composition.

35 Method of Using Topical Personal Care Compositions

The compositions of the present invention are used in conventional ways to provide the desired benefit appropriate to the product such as hair styling, holding,

cleansing, conditioning and the like for hair care compositions and benefits such as moisturization, sun protection, anti-acne, anti-wrinkling, artificial tanning, analgesic, and other cosmetic and pharmaceutical benefits for skin care compositions. Such methods of use depend upon the type of composition employed but generally involve application of an effective amount of the product to the hair or skin, which may then be rinsed from the hair or skin (as in the case of shampoos and some conditioning products) or allowed to remain on the hair (as in the case of spray, mousse, or gel products), or allowed to remain on the skin (as in the case of the skin care compositions). By "effective amount" is meant an amount sufficient to provide the benefit desired. Preferably, hair rinse, mousse, and gel products are applied to wet or damp hair prior to drying and styling of the hair. After such compositions are applied to the hair, the hair is dried and styled in the usual ways of the user. Hair sprays are typically applied to dry hair after it has already been dried and styled. Cosmetic and pharmaceutical topical skin care compositions are applied to and rubbed into the skin.

The following examples further illustrate preferred embodiments within the scope of the present invention. The examples are given solely for the purposes of illustration and are not to be construed as limitations of the present invention as many variations of the invention are possible without departing from its spirit and scope.

EXPERIMENTAL

Silicone macromers I and II and Polymers I, II, and III, can be synthesized according following procedures. There are numerous variations on these procedures which are entirely up to the discretion of the synthetic chemist (e.g., choice of degassing method and gas, choice of initiator type, extent of conversion, reaction loading, etc). The choice of initiator and solvent are often determined by the requirements of the particular monomers used, since different monomers have different solubilities and different reactivities to a specific initiator.

Synthesis of 1-(Dimethylchlorosilyl)-2-(p-styryl)ethane End-Cap

In a three neck round bottom flask equiped with a magnetic stirrer, a thermometer and an addition funnel, a solution of divinyl benzene (50.0g, 0.384 moles) and chlorodimethyl silane (11.113 g, 0.128 moles) is prepared in dry tetrahydrofuran (THF) (200 mL). To this solution, a chloroplatinic acid solution (0.150 g in 20 mL THF) is added dropwise. The reaction is highly exothermic, hence a slow addition of chloroplatinic acid is necessary. After the addition of platinic acid, the reaction is allowed to continue for an additional one hour, with stirring. This solution (10.64 M) is used to prepare styrene end-capped silicone macromer I, as described below.

Silicone Macromers I and II: In a round bottom flask which is equipped with a magnetic stirrer, a solution of hexamethylcyclotrisiloxane monomer (150 g) is prepared in dry cyclohexane (150 g). sec-Butyl lithium (0.0125 moles) initiator is added dropwise. The reaction mixture is allowed to stir for 10 minutes. This step is followed by the addition of THF (150 g) to the reaction mixture. The solution is stirred overnight, followed by heating at 50 deg C for 5 hours. The end-cap (0.025 moles) is then added slowly to the solution. Silicone Macromer I is made with the 1-(Dimethylchlorosilyl)-2-(p-styryl)ethane end-cap, as prepared above. The end-cap solution of the above end-cap synthesis is added dropwise. Silicone Macromer II is made with a chlorodimethylstyrylsilane end-cap, which can be prepared as described and shown in Holohan, George, Barrie, and Parker, "Monofunctional Polydimethylsiloxane Oligomers For Graft Copolymerization", Macromol. Chem. Phys. 195, 2965-2979 (1994). The end-cap from this synthesis is added dropwise to the solution. Alternately, the end-cap can be solubilized in THF and then added dropwise. The macromer is recovered by precipitating the final solution in methanol.

Polymer I: Place 20 parts acrylic acid, 63 parts t-butylacrylate, and 17 parts styrene end-capped polydimethylsiloxane macromer(Silicone Macromer I) in a flask. Add sufficient ethyl acetate or acetone (preferably acetone) as the reaction solvent to produce a final monomer concentration of 25%. Add initiator, azobisisobutyronitrile, to a level of 0.5% by weight relative to the amount of monomer. Purge the flask of oxygen by inserting an argon gas line below the surface of the liquid and allowing argon to bubble into the reaction solvent for about 15 minutes. Heat to 60°C and maintain this temperature for 48 hours while agitating. Terminate the reaction by cooling to room temperature, and dry off the reaction solvent by pouring the reaction mixture into a teflon-coated pan and placing in a vacuum oven.

Polymer II: Place 20 parts acrylic acid, 63 parts t-butylacrylate, and 17 parts styrene end-capped polydimethylsiloxane macromer(Silicone Macromer II) in a flask. Add sufficient ethyl acetate or acetone (preferably acetone) as the reaction solvent to produce a final monomer concentration of 25%. Add initiator, azobisisobutyronitrile, to a level of 0.5% by weight relative to the amount of monomer. Purge the flask of oxygen by inserting an argon gas line below the surface of the liquid and allowing argon to bubble into the reaction solvent for about 15 minutes. Heat to 60°C and maintain this temperature for 48 hours while agitating. Terminate the reaction by cooling to room temperature, and dry off the

reaction solvent by pouring the reaction mixture into a teflon-coated pan and placing in a vacuum oven.

- Polymer III:** Place 20 parts acrylic acid, 30 parts N-isopropylacrylamide, 35 parts t-butylacrylate, and 15 parts styrene end-capped polydimethylsiloxane macromer (Silicone Macromer I) in a flask. Add sufficient ethyl acetate or acetone (preferably acetone) as the reaction solvent to produce a final monomer concentration of 25%. Add initiator, azobisisobutyronitrile, to a level of 0.5% by weight relative to the amount of monomer. Purge the flask of oxygen by inserting an argon gas line below the surface of the liquid and allowing argon to bubble into the reaction solvent for about 15 minutes. Heat to 60°C and maintain this temperature for 48 hours while agitating. Terminate the reaction by cooling to room temperature, and dry off the reaction solvent by pouring the reaction mixture into a teflon-coated pan and placing in a vacuum oven.

EXAMPLES

- The following examples further describe and demonstrate embodiments within the scope of the present invention. The examples are given solely for the purpose of illustration and are not to be construed as limitations of the present invention, as many variations thereof are possible without departing from the spirit and scope of the invention. Ethanol in the following formulas is anhydrous, unless otherwise indicated.

EXAMPLES 1-4

Disclosed below are exemplary mousse compositions of the present invention.

	<u>Component (wt.%)</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
5	Polymer III	3.00	3.00	3.00	3.00
	Lauramine-oxide	0.10	0.10	0.00	0.10
	Cocamidopropyl betaine	1.33	1.33	0.30	1.33
	Propylene glycol	0.20	0.10	0.10	0.10
	Perfume	0.10	0.10	0.05	0.10
10	Disodium EDTA - dihydrate	0.10	0.10	0.10	0.10
	Phenoxyethanol	0.25	0.25	0.25	0.25
	Methyl paraben	0.15	0.15	0.15	0.15
	Polyquaternium-4 ¹	0.00	0.00	0.00	0.20
	Stearyltrimethylammonium				
15	chloride	0.00	0.00	0.20	0.00
	KOH Solution (45% active)	0.80	0.80	1.00	0.90
	Deionized Water	q.s.	q.s.	q.s.	q.s.

¹Celquat L200, National Starch and Chemical Corp. (Bridge water, NJ, USA,
20 copolymer of hydroxyethylcellulose and diallyldimethyl ammonium chloride.

The composition is made by mixing the silicone grafted copolymer in the water, with the KOH solution, then sequentially adding the remaining ingredients, except for perfume, with stirring, heating to 40°C - 60°C with stirring, and stirring for an
25 additional period of about eight hours while allowing the composition to cool at ambient temperature, and then mixing in the perfume. The product can then be packaged in a conventional aerosol or non aerosol mousse spray package.

EXAMPLES 5-8

Below are several exemplary reduced VOC hair spray compositions of the
30 present invention.

	<u>Component (wt.%)</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>
	Polymer I or II	4.50	3.50	4.00	3.00
	Deionized Water	5.00	3.00	18.00	17.00
	Isododecane	1.50	0.00	0.00	0.00
35	KOH Solution (45% active)	0.90	0.65	0.00	0.75
	NaOH Solution (30% active)	0.00	0.00	1.00	0.00
	Triethyl Citrate	0.20	0.40	0.00	0.10

	Perfume	0.10	0.25	0.05	0.10
	Propylene Glycol	0.05	0.00	0.00	0.10
	N-Butane (Propellant)	7.50	6.00	0.00	0.00
	HFC 152A (Propellant)	15.00	17.00	0.00	0.00
5	Dibutyl Adipate	0.00	0.00	0.30	0.00
	SDA 40 Ethanol	qs	qs	qs	qs

10 The compositions are made by adding the ethanol to a mixing container first, followed by addition of the rest of the non-propellant ingredients sequentially in the order shown above, followed by vigorous stirring for two to three hours. The compositions of Examples 5 and 6 are then added to conventional aerosol cans in the conventional manner and charged with the propellants. The compositions of Examples are added to conventional nonaerosol pump spray containers.

15

EXAMPLE 9

The following is a shampoo composition representative of the present invention.

	<u>Component</u>	<u>Weight %</u>
20	Ammonium laureth sulfate	5.00
	Cocamido propyl betaine	6.00
	Polymer III	4.00
	NaOH Solution (30% active)	0.10
	PEG 150 distearate	2.00
25	Glydant ¹	0.38
	Aminomethylpropanol	0.40
	Perfume	1.00
	Deionized Water	q.s.

¹Preservative commercially available from Glyco, Inc.

30 The shampoo is prepared by combining the ammonium laureth sulfate and Silicone Grafted Copolymer (Polymer III) and heating to 70°C for about 1/2 hour with mixing. The remaining ingredients are added and mixed for an additional 1/2 hour. The batch is then cooled to ambient temperature. The pH is adjusted to 6.5 by the addition of citric acid or sodium hydroxide, if necessary.

EXAMPLE 10

The following is a styling and conditioning hair rinse composition representative of the present invention.

	<u>Component</u>	<u>Weight %</u>
5	Polymer III	3.00
	NaOH Solution (30% active)	0.90
	<u>Silicone Premix</u>	
	Silicone Gum GE SE76 ¹	0.50
	Decamethyl cyclopentasiloxane	4.00
10	<u>Main Mix</u>	
	Cetyl hydroxyethylcellulose ²	0.60
	Locust bean gum	0.50
	EDTA, disodium salt	0.15
	DTDMAC	0.65
15	Glydant ³	0.40
	Deionized Water	q.s.

¹Commercially available from General Electric

²Polysurf from Aqualon Co.

³Preservative commercially available from Glyco, Inc.

20 The Silicone Premix is blended separately by conventional means. The Main Mix is prepared by adding all the ingredients and heating to 95°C for 1/2 hour with agitation. As the batch is cooled to about 60°C, the Silicone Premix, Silicone Grafted Copolymer (Polymer III), and NaOH solution are added to the Main Mix with agitation and the batch is cooled to ambient temperature.

25

EXAMPLE 11

Reduced VOC hairspray compositions are prepared from the following components.

<u>Ingredients</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>
Water	QS 100	QS 100	QS 100	QS 100
Ethanol	54.0	54.0	54.0	54.0
Polymer I, II, or III	4.0	3.0	4.0	3.0
KOH Solution (45% active)	0.80	0.60	1.00	0.75
Dioctyl Phthalate	0.40	---	0.10	---
Fragrance	0.05	0.2	---	---

- These products are prepared by first dissolving the polymer in the ethanol with stirring. The remaining ingredients are then added with stirring. The resulting hair spray compositions can then be packaged in a nonaerosol spray pump. Alternatively, the compositions can be combined with conventional propellants and packaged in an aerosol spray container.

EXAMPLE 12

Mousse compositions are prepared from the following components utilizing conventional mixing techniques.

10

<u>Ingredients</u>	<u>Weight %</u>		
	<u>A</u>	<u>B</u>	<u>C</u>
Water	QS 100	QS 100	QS 100
Polymer III	3.00	2.50	3.50
NaOH Solution (30% active)	0.80	0.50	0.90
Lauramide DEA	0.33	0.33	0.33
Sodium Methyl Oleyl Taurate	1.67	1.67	1.67
DMDM Hydantoin	0.78	0.78	0.78
Disodium EDTA	0.20	0.20	0.20
Polyoxyalkylated isostearyl alcohol ¹	0.10	0.10	0.10
Fragrance	0.10	0.10	0.10
Propellant ²	7.0	7.0	7.0

- These products are prepared by first dissolving the polymer in water with stirring. The remaining ingredients, except the propellant, are then added with stirring. The resulting mousse concentrate can then be combined with conventional propellants (e.g., Propellant A46²) and packaged in an aerosol spray. These mousses are useful for application to the hair to provide a styling and holding benefit.

¹ Aerosurf 66-E10.

² Available as a mixture of 82.46% isobutane, 16.57% propane, and 0.001% butane.

EXAMPLE 13

Hair tonic compositions are prepared from the following components utilizing conventional mixing techniques.

<u>Ingredients</u>	<u>Weight %</u>		
	<u>A</u>	<u>B</u>	<u>C</u>
Ethanol (190 Proof)	QS 100	QS 100	QS 100
Polymer I, II, or III	0.75	1.00	1.25
Aminomethyl Propanol	0.15	0.18	0.22
Fragrance	0.10	0.20	0.30

- 5 These products are prepared by dissolving the polymer in the ethanol with stirring and then adding the fragrance and any colors. These hair tonics are useful for application to the hair to provide a styling and holding benefit.

EXAMPLE 14

- 10 A conditioning and styling shampoo composition is prepared from the following components utilizing conventional mixing techniques.

	<u>Ingredients</u>	<u>Weight %</u>
	<u>Styling Agent</u>	
	Polymer III	3.00
15	NaOH Solution (30% active)	0.20
	<u>Premix</u>	
	Silicone gum	0.50
	Dimethicone, 350 cs fluid	0.50
	<u>Main Mix</u>	
20	Water	QS100
	Ammonium lauryl sulfate	11.00
	Cocamide MEA	2.00
	Ethylene glycol distearate	1.00
	Xanthan Gum	1.20
25	Methylchloroisothiazolinone (and)	
	methylisothiazolinone	0.04
	Citric Acid to pH 4.5 as needed	

- 30 The Main Mix is prepared by first dissolving the xanthan gum in the water with conventional mixing. The remaining Main Mix ingredients are added and the Main

- Mix is heated to 150⁰F with agitation for 1/2 hour. The Styling Agent and the Premix are then added sequentially with about 10 minutes of agitation between additions, and the entire mixture is stirred while the batch is cooled to room temperature. For varied particile size, the Styling Agent and Premix can be added at different times using either or both high shear mixing or normal agitation.

EXAMPLE 15

Anti-Acne Composition

An anti-acne composition is made by combining the following components using conventional mixing technology.

10	<u>Ingredient</u>	<u>Weight %</u>
	Water	QS100
	Salicylic Acid	2.00
	Polymer I, II, or III	2.00
	Ethanol (SDA 40)	40.00
15	Aminomethyl Propanol	0.40

EXAMPLE 16

A topical analgesic composition is made by combining the following ingredients utilizing conventional mixing techniques.

20	<u>Ingredient</u>	<u>Weight %</u>
	Water, Purified	QS100
	Ibuprofen	2.00
	Polymer III	2.00
	Aminomethyl Propanol	0.45
25	Ethanol (SDA 40)	20.00

EXAMPLE 17

A composition for sunless tanning is made by combining the following ingredients utilizing conventional mixing techniques.

	<u>Ingredients</u>	<u>Weight %</u>
30	<u>Phase A</u>	
	Water	qs 100
	Polymer III	2.00
	NaOH Solution (30% active)	0.70

	Carbomer 934 ¹	0.20
	Carbomer 980 ²	0.15
	Acrylic Acid Copolymer ³	0.15
	<u>Phase B</u>	
5	PPG-20 Methyl Glucose Ether	
	Distearate	2.00
	Tocopheryl Acetate	1.20
	Mineral Oil	2.00
	Stearyl Alcohol	1.00
10	Shea Butter	1.00
	Cetyl Alcohol	1.00
	Ceteareth-20	2.50
	Ceteth-2	1.00
	Ceteth-10	1.00
15	<u>Phase C</u>	
	DEA-Cetyl Phosphate	0.75
	<u>Phase D</u>	
	Dihydroxyacetone	3.00
20	<u>Phase E</u>	
	Butylene Glycol	2.00
	DMDM Hydantoin (and)	
	Iodopropynyl Butylcarbamate	0.25
	<u>Phase F</u>	
25	Fragrance	1.00
	Cyclomethicone	2.00

In a suitable vessel the Phase A ingredients are dispersed in the water and heated to 75-85^o C. In a separate vessel the Phase B ingredients are combined and heated to 85-90^o C until melted. Next, the DEA-Cetyl Phosphate is added to the liquid Phase B and stirred until dissolved. This mixture is then added to Phase A to form the emulsion. The emulsion is cooled to 40-45^o C with continued mixing. Next, in a separate vessel, the dihydroxyacetone is dissolved in water and the

resulting solution is mixed into the emulsion. In another vessel, the Phase E ingredients are heated with mixing to 40-45°C until a clear solution is formed and this solution is then added to the emulsion. Finally, the Phase F ingredients are added to the emulsion with mixing, which is then cooled to 30-35°C, and then to room temperature. This emulsion is useful for topical application to the skin to provide an artificial tan.

- 1 Available as Carbopol^R 934 from B.F. Goodrich.
- 2 Available as Carbopol^R 980 from B.F. Goodrich.
- 3 Available as Pemulen TR1 from B.F. Goodrich.

10

EXAMPLE 18**Sunscreen Composition**

An oil-in-water emulsion is prepared by combining the following components utilizing conventional mixing techniques.

	<u>Ingredients</u>	<u>Weight %</u>
15	<u>Phase A</u>	
	Water	QS100
	Carbomer 954 ¹	0.24
	Carbomer 1342 ²	0.16
	Polymer III	1.75
20	NaOH (30%)	0.70
	Disodium EDTA	0.05
	<u>Phase B</u>	
	Isoarachidyl Neopentanoate ³	2.00
	PVP Eicosene Copolymer ⁴	2.00
25	Octyl Methoxycinnamate	7.50
	Octocrylene	4.00
	Oxybenzone	1.00
	Titanium Dioxide	2.00
	Cetyl Palmitate	0.75
30	Stearoxytrimethylsilane	
	(and) Stearyl Alcohol ⁵	0.50
	Glyceryl Tribehenate ⁶	0.75

		Dimethicone	1.00
		Tocopheryl Acetate	0.10
		DEA-Cetyl Phosphate	0.20
		<u>Phase C</u>	
5		Water	2.00
		Triethanolamine 99%	0.60
		<u>Phase D</u>	
		Water	2.00
		Butylene Glycol	2.00
10		DMDM Hydantoin (and)	
		Iodopropynyl Butylcarbamate ⁷	0.25
		dL Panthenol	1.00
		<u>Phase E</u>	
		Cyclomethicone	1.00
15	1	Available as Carbopol ^R 954 from B.F. Goodrich.	
	2	Available as Carbopol ^R 1342 from B.F. Goodrich.	
	3	Available as Elefac I-205 from Bernel Chemical.	
	4	Available as Ganex V-220 from GAF Corporation.	
	5	Available as DC 580 Wax from Dow Corning.	
20	6	Available as Synchronwax HRC from Croda.	
	7	Available as Glydant Plus from Lonza.	

In a suitable vessel the Phase A ingredients are dispersed in the water and heated to 75-85° C. In a separate vessel the Phase B ingredients (except DEA-Cetyl Phosphate) are combined and heated to 85-90° C until melted. Next, the DEA-Cetyl Phosphate is added to the liquid Phase B and stirred until dissolved. This mixture is then added to Phase A to form the emulsion. The Phase C ingredients are combined until dissolved and then added to the emulsion. The emulsion is then cooled to 40-45° C with continued mixing. In another vessel, the Phase D ingredients are heated with mixing to 40-45° C until a clear solution is formed and this solution is then added to the emulsion. Finally, the emulsion is cooled to 35° C and the Phase E ingredient is added and mixed. This emulsion is useful for topical application to the skin to provide protection from the harmful effects of ultraviolet radiation.

EXAMPLE 19**Facial Moisturizer**

A leave-on facial emulsion composition is prepared by combining the following components utilizing conventional mixing techniques.

5	<u>Ingredient</u>	<u>Weight %</u>
	Water	QS100
	Polymer III	1.00
	NaOH Solution (30% active)	0.40
	Glycerin	3.00
10	Cetyl Palmitate	3.00
	Cetyl Alcohol	1.26
	Quaternium-22	1.00
	Glyceryl Monohydroxy Stearate	0.74
	Dimethicone	0.60
15	Stearic Acid	0.55
	Octyldodecyl Myristate	0.20
	Carbomer 1342	0.125
	Tetrasodium EDTA	0.10
	DMDM Hydantoin and Iodopropynyl	
20	Butyl Carbamate	0.10
	Carbomer 951	0.075

25

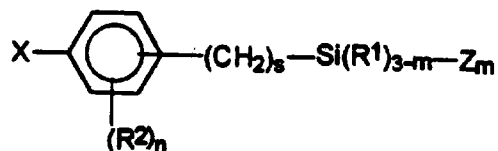
WHAT IS CLAIMED IS:

1. A topical personal care composition containing silicone grafted copolymer having improved resistance against hydrolysis, said composition being suitable for topical application to the skin or hair, and comprising:

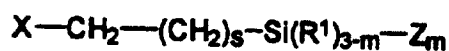
(a) from 0.1% to 50%, by weight of the composition, of silicone grafted copolymer containing:

(i) from 1% to 99%, by weight of the copolymer, of acid-containing monomers;

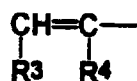
(ii) from 1% to 50%, by weight of the copolymer, of styrene end-capped or alkenyl end-capped silicone macromer having the formulas, respectively:



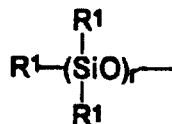
or



wherein: *s* is an integer from 0 to 6; *m* is an integer from 1 to 3, R² is C1-C10 alkyl or C7-C10 alkylaryl; *n* is an integer from 0 to 4; X is an ethylenically unsaturated group of the formula :



wherein R³ is -H or C1-C6 alkyl; R⁴ is H or C1-C6 alkyl; Z is



wherein each R¹ independently is an alkyl, aryl or alkylaryl having from 1 to 10 carbon atoms, and *r* is an integer from 4 to 700; and combinations thereof;

(iii) from 0% to 98% of additional monomers; and combinations thereof; and

(b) from 1% to 99.9%, by weight of the composition, of an aqueous or hydroalcoholic solvent for said silicone grafted copolymer suitable for application to the hair or skin, wherein said copolymer is soluble or dispersible in said solvent.

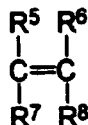
2. A composition as in Claim 1, wherein said silicone macromer is the styrene end-capped silicone macromer, n is 0, and said $-(CH_2)_s-Si(R^1)_3-Z_m$ of said silicone macromer is substituted at the para position relative to X wherein s is from 0 to 2, m is 1, n is 0, R^3 is H, R^4 is H or CH_3 , and R^1 is an alkyl, preferably wherein R^1 is methyl and r is from 50 to 500.

3. A composition according to any preceding Claim wherein said copolymer comprises from 1% to 50%, by weight of the copolymer, of said additional monomers, said additional monomers being nonionic, cationic, amphoteric, or a combination thereof, preferably wherein said additional monomers are nonionic monomers selected from the group consisting of acrylic and methacrylic acid esters of C1-C24 alcohols; styrene; alkylstyrenes; chloro-styrene; vinyl esters; vinyl chloride; vinyl toluene; vinyl caprolactam; vinylidene chloride; acrylonitrile; alpha-alkylstyrenes; 1,3-dialkenes; ethylenically monounsaturated hydrocarbons; alkoxyalkyl (meth)acrylates; alkyl vinyl ethers; di-acrylates and di-methacrylates; acrylamide; methacrylamide; diacetonacrylamide; N,N-dialkyl(meth)acrylamides; N-alkyl(meth)acrylamides; acrylate and methacrylate alcohols; vinyl pyrrolidone; allyl alcohol; vinyl alcohol; and combinations thereof.

4. A composition according to any preceding Claim wherein said acid-containing monomers are selected from the group consisting of carboxylic acids and sulfonic acids.

5. A composition as in any preceding Claim wherein said acid-containing monomers are carboxylic acids.

6. A composition as in any preceding Claim wherein said carboxylic acid monomers are selected from the group consisting of those corresponding to the formula:



wherein: R⁵ and R⁶ independently are H or C1-C6 alkyl; R⁷ is H, C1-C6 alkyl, or a carboxylic moiety having up to 12 carbon atoms; and R⁸ is a carboxylic moiety having up to 12 carbon atoms; and mixtures thereof.

7. A composition as in any preceding Claim wherein said copolymer comprises:
 - (i) from 5% to 90%, by weight of said copolymer, of said acid-containing monomers;
 - (ii) from 2% to 40%, by weight of said copolymer, of said silicone macromers;
 - (iii) from 0% to 70%, by weight of said copolymer, of said additional monomers.
8. A composition as in any preceding Claim wherein said copolymer comprises:
 - (i) from 10% to 75%, by weight of said copolymer, of said acid-containing monomers;
 - (ii) from 5% to 40%, by weight of said copolymer, of said silicone macromers;
 - (iii) from 5% to 70%, by weight of said copolymer, of said additional monomers.
9. A composition as in any preceding Claim wherein said copolymer comprises:
 - (i) from 15% to 50%, by weight of said copolymer, of said acid-containing monomers;
 - (ii) from 5% to 25%, by weight of said copolymer, of said monomers derived from said silicone monomers;
 - (iii) from 40% to 70%, by weight of said copolymer, of said additional monomers.
10. A hair spray product comprising the composition of any preceding Claim disposed within an aerosol or nonaerosol spray container.

INTERNATIONAL SEARCH REPORT

Intern. al Application No
PCT/US 96/04183

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A61K7/06 A61K7/48

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 412 770 (MINNESOTA MINING & MFG) 13 February 1991 see claims 1-7 see page 4, line 55 - page 5, line 11 see page 5, line 55 - page 6, line 2 ---	1,3,4
X	WO,A,95 00108 (PROCTER & GAMBLE ;WELCH ROSEMARY JANE (GB); MARCHANT PHILIP JOHN () 5 January 1995 see claims 1-6 ---	1-7
A	WO,A,95 04518 (PROCTER & GAMBLE) 16 February 1995 see claim 1 see page 7, line 23 - page 10, line 25 ---	1,3-6
A	WO,A,93 23446 (PROCTER & GAMBLE) 25 November 1993 -----	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- * "A" document defining the general state of the art which is not considered to be of particular relevance
- * "E" earlier document but published on or after the international filing date
- * "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- * "O" document referring to an oral disclosure, use, exhibition or other means
- * "P" document published prior to the international filing date but later than the priority date claimed

* "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

* "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

* "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

* "&" document member of the same patent family

Date of the actual completion of the international search

10 September 1996

Date of mailing of the international search report

20.09.96

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+ 31-70) 340-3016

Authorized officer

McConnell, C

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internal Application No

PCT/US 96/04183

PC1/US 90/04183

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0412770	13-02-91	US-A- 4981903	01-01-91
		AU-A- 5185293	27-01-94
		AU-A- 5918990	07-02-91
		CA-A- 2021570	08-02-91
		DE-D- 69022800	09-11-95
		DE-T- 69022800	15-05-96
		JP-A- 3081311	05-04-91
		JP-B- 7074256	09-08-95
		US-E- RE34958	30-05-95
		US-A- 5021477	04-06-91

WO-A-9500108	05-01-95	AU-A- 6910194	17-01-95
		BR-A- 9406849	16-04-96
		CA-A- 2165431	19-12-94
		EP-A- 0723433	31-07-96

WO-A-9504518	16-02-95	AU-A- 7336694	28-02-95
		CA-A- 2167483	16-02-95
		EP-A- 0712309	22-05-96
		FI-A- 960494	02-04-96
		NO-A- 960451	02-04-96

WO-A-9323446	25-11-93	AU-A- 4243393	13-12-93
		CA-A- 2135186	25-11-93
		CN-A- 1081195	26-01-94
		CZ-A- 9402773	16-08-95
		EP-A- 0640105	01-03-95
		FI-A- 945358	14-11-94
		HU-A- 70074	28-09-95
		JP-T- 7508060	07-09-95
		NO-A- 944303	13-01-95
		SK-A- 136194	09-08-95
